THE UNIVERSITY OF ALBERTA

EVALUATION OF OZONE, CHLORINE DIOXIDE, AND GRANULAR ACTIVATED CARBON, FOR TASTE AND ODOUR CONTROL

by

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(C)

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ABSTRACT

Taste and odour are two important parameters determining water quality and the effectiveness of water treatment systems. The City of Edmonton draws its drinking water from the North Saskatchewan River. The taste and odour problems for the City's Rossdale Water Treatment Plant originated from the plant being located down stream from the storm sewer outfalls. Waste chemical products, accumulated during the long winter months, tax the otherwise capable treatment facilities.

As a joint research venture, the City of Edmonton and the University of Alberta established a pilot plant project at the Rossdale Water Treatment Plant to study the reduction of the organics in the water. A thorough literature review was prepared as one of the first steps in treating the problem. The review included the understanding of the olfactory and sensory systems, and the current theories in the relationship between chemical structures and their taste and odour causing abilities. The biological causes of taste and odour were also presented in depth, even though they do not seem to be a major contributor to the problem for the City. Taste and odour causing chemicals were also discussed.

Based on the study, the use of ozone, chlorine dioxide and granular activated carbon (GAC) was examined for their effectiveness in the removal of trace organics of health and organoleptic concern. These processes were deemed to be the most effective and amenable to large scale implementation for the City. Using a factorial design experiment, the two oxidants were applied at dosages of 0.5, 1.0 and 2.0 mg/L, each at a contact time of 30 and 60 minutes. The effluent then entered the corresponding GAC columns in an upflow mode. River water fed into the pilot plant was spiked with a selected organic compound to permit quantitative comparisons. Ethylbenzene, a priority pollutant, which was found in the raw and treated water, was applied at a concentration of 125 ug/L. The effects of various treatments were then analyzed using gas chromatography.

Analysis of Variance (ANOVA) method indicated that ozone provided greater reduction of ethylbenzene than chlorine dioxide at 2 mg/L and 30 minutes contact time. Removal by ozone also increased steadily with increased dosage. As expected, carbon adsorption following either oxidant provided significant further reduction.

Ongoing studies on other surrogate chemicals are being conducted to determine the effectiveness of the various systems.

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LIST OF SYMBOLS, ABBREVIATIONS AND SYNONYMS

A°	Angstrom
ANOVA	Analysis of Variance
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
BAC	Biological activated carbon
BOD	Biochemical oxygen demand
C	Centigrade
CAE	Carbon-Alcohol extract
CCE	Carbon-Chloroform extract
Cl_2	Chlorine
ClO_2	Chlorine dioxide
ClO_2^-	Chlorite
ClO_3^-	Chlorate
COD	Chemical oxygen demand
CSF	Coagulation-Sedimentation-Rapid sand filtration
DOC	Dissolved organic carbon
GAC	Granular activated carbon
GC	Gas chromatography
g	Gram
G-6-PD	Glucose-6-Phosphate Dehydrogenase
h	Hour
kg	kilogram
km	kilometre
L	Litre
LD_{50}	Lethal dose in 24 hour of a chemical for 50% of experimental animal (mg/kg)
Lpm	Litre per minute
MIB	Methylisoborneol
MS	Mass Spectrometer
mg	milligram
mL	millilitre
mm	millimetre
ML/d	Million litre per day
ppm	parts per million
ppb	parts per billion
PAH	Polycyclic aromatic hydrocarbons
PAC	Powdered activated carbon
O_3	Ozone
OII	Odour Intensity Index
ON	Odour Number
OTC	Odour Threshold Concentration
OTU	Odour Threshold Unit
TCU	True Colour Unit
TLV	Threshold Limit Value
TO	Threshold Odour
TOC	Total organic carbon
TOCl	Total organic chlorine
TON	Threshold Odour Number
THM	Trihalomethanes
TTC	Taste Threshold Concentration
UV	Ultraviolet
USEPA	United States Environmental Protection Agency
USPHS	United States Public Health Service
v	Voltage
WHO	World Health Organization
WPCF	Water Pollution Control Federation
ug/L	microgram per Litre. 1ppb= 1ug/L

I. INTRODUCTION

The City of Edmonton Water and Sanitation Department is responsible for providing potable water to approximately 700,000 consumers within the City and neighbouring communities. THe City services the majority of the population residing within a 50 km radius, but also includes the Town of Vegreville, about 100 km east of Edmonton (City of Edmonton, 1984).

The City has a total of four plants at two different sites. The three plants at Rossdale were constructed in 1947, 1956 and 1965, while the E. L. Smith Plant was commissioned in 1976. In this thesis, the Rossdale facilities are referred to as a single plant. In 1983, the plants had an annual mean production of 318 ML/d with 63.9% being processed at the Rossdale Water Treatment Plant. Both treatment sites used similar treatment processes consisting of coagulation, flocculation, sedimentation, lime softening, recarbonation, fluoridation, chloramination and filtration. Polyelectrolytes and powdered activated carbon are used when needed. Alum sludge is disposed of in the North Saskatchewan River, lime sludge at the Clover Bar Landfill site.

Raw water is withdrawn from the North Saskatchewan River for processing, upstream from the sewage treatment plant. The present water treatment facilities are normally effective in removing pollutants in the water. However, ice breakup and excessive surface runoff during the spring and summer wash many organic products into the river. The resulting degradation of river water quality poses a problem for the Rossdale Water Treatment Plant since it is located downstream from many storm sewer system outfalls. The extra burden can produce some taste and odour problems in the area serviced by the Rossdale Water Treatment Plant. A study by Masuda in 1971 had found a Threshold Odour Number (TON)[1] level as high as 100 and 32 during April and June of 1970, respectively, in the raw water. Analyses of phenols, oil and grease, and microorganisms were non-conclusive in determining the cause of the odour (Masuda, 1971). The taste and odour problem in Edmonton may have stemmed from river contamination of natural and anthropogenic origins. Some of the possible causes include phenolics, which become halogenated, and street runoff (petrochemicals). Other industrial

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[1] TON: As an odourous gas or vapour is diluted with air or water, a point is finally reached when, on further dilution, the odour can no longer be detected. The minimum concentration is called the Threshold Odour Number

chemicals and microbial metabolites have also been suspected (Walker, 1983).

GC-MS analysis on the runoff water in 1982 identified many organic compounds in the raw and treated water. Some of these are known taste and odour causing compounds, and are classified as 'priority pollutants' by the U.S. EPA (Rice, 1981; Walker, 1983).

With increasing consumer demand for better water quality and more stringent water quality standards, there is a need to provide better technology at the Rossdale Water Treatment Plant, capable of removing trace pollutants more effectively.

As a joint research venture, the City of Edmonton and the University of Alberta established a pilot plant project at the Rossdale Water Treatment Plant. The initial project activity (May to October, 1982) was a thorough literature review of the nature of taste and odour in water, and the technology for its removal. On the basis of the review, the following three treatment operations were selected for evaluation: chlorine dioxide, ozone and granular activated carbon.

A pilot plant was constructed and placed in operation in March 1983. This thesis describes the first 26 weeks of the pilot plant operation (March to September, 1983). During this period, the following tests were conducted :

March to May :

- Prelimary system shakedown without a coagulation step in the pilot plant
- Testing of chlorine dioxide, ozone, and granular activated carbon with partially treated spring runoff water

May to June :

- Factorial experiments to determine the optimal coagulation-flocculation conditions to be used in the pilot plant

June to July :

- System shakedown with a coagulation step using raw water

July to August :

- Initial study of the first surrogate taste and odour causing chemical, ethylbenzene. This included bench testing, a volatilization study, a coagulation study and control runs

August to September :

- Factorial experiments to determine the optimal oxidant dosage and contact time for the reduction of ethylbenzene.
- comparision of GAC removal with or without oxidants

Other taste and odour causing chemicals, such as *n*-decane and chlorinated phenols will also be tested in the future, as individual compounds or as a mixture.

II. PROJECT OBJECTIVE

The objective of this pilot plant project was to determine the effectiveness of various treatment methods in reducing taste and odour in the City of Edmonton's water. Following a literature review, pilot trains were set up to compare the effectiveness of chlorine dioxide, ozone and granular activated carbon with runoff water and water spiked with various taste-and-odour-causing chemicals. The six systems studied in the pilot plant included:

1. coagulation
2. chlorine dioxide
3. chlorine dioxide-granular activated carbon
4. ozone
5. ozone-granular activated carbon
6. granular activated carbon only

It was the aim of the project to produce meaningful data that could be extracted and used for future investigation or as a first step towards the application of some or all of the processes in the Treatment Plants. Surrogate chemicals were used to give a better indication as to the reaction dynamics and by-products formed with the oxidant and adsorbant. The data may be used to estimate and understand the removal of classes of organics.

Chemical parameters were monitored on a regular basis. This served to determine to what extend the taste and odour causing chemicals were being removed by different unit processes. Optimization studies were also conducted to determine if treatment could be improved by the control of process variables such as dosage and contact time. Two different types of granular activated carbon were used to allow for comparision.

III. LITERATURE REVIEW

A. Taste and Odour in Water Supplies

The senses of taste and smell are employed by most, if not all animals, not only for the purpose of food selection, but more importantly, to detect life-threatening hazards in their environment. Moncrieff (1967) suggested that there is no naturally occurring toxic vapour that is odourless and quoted Richter (1950):

> "Tasteless toxic substances could not have existed widespread in nature in readily available forms at any time in evolutionary history, since in the absence of a taste warning, every animal or man that ingested them could have perished. It is more likely that they belong to a group of compounds to which in evolutionary history man and animals have never been extensively exposed."

Although this statement may no longer be true in light of all the new synthetic, odourless but sometimes toxic compounds generated by man and his activities, it is still an important objective for any water treatment plant, to provide a water to the consumer that has no adverse taste and odour. The importance of the sensory aspects of water quality is summarized in a 1971 World Health Organization statement : "Coolness, absence of turbidity, and absence of colour and any disagreeable taste and smell are of the utmost importance in public supplies of drinking water."

There are many reports relating taste-and-odour-causing compounds to toxicity. Rosen (1975) found that many of the toxic chemicals listed in the *Safe Drinking Water Act* of 1974 were discovered through taste and odour research. This is because the high electron density sites in the molecules, which are responsible for odour, usually manifest some degree of toxicity (Nebel and Forde, 1975). Drinking water standards in the U.S.S.R. are based on the taste and odour thresholds which are more restricted than the toxicity limits (Zoeteman, 1974; Rosen, 1975).

The problem of taste and odour is very complex because the senses of taste and odour are intimately related, and their responses are often difficult to differentiate clearly. Most individuals have a more acute sense of smell than taste. In many instances, minute concentrations of some compounds are more readily detected by odour than by

conventional analytical methods. Therefore, a laboratory must depend on human subjects for odour analyses.

In their 1968 report, an AWWA committee found odour to be the major problem in water. Taste, as a specific process, is rarely a problem in water supplies. As early as 1956, taste and odour were considered to be one problem (Symons, 1956). Studies have emphasized odour since taste is often indistinguishable from or is a function of odour (Baker, 1961). However, certain non-volatile substances dissolved in water can cause tastes without causing odour. The terms "Taste" and "Odour" are used jointly in the vernacular of water terminology.

A more recent report by Zoeteman (1980) found that despite the sensory detection of chemicals, some compounds such as chloroform and trichloroethene, cannot be perceived in water at concentrations which may increase the risk of cancer. The sensory system is more effective when a wide range of substances are presented than for a single source. He concluded that the absence of any adverse taste and odour does not guarantee the safety of drinking water, but impaired taste is often associated with toxic or carcinogenic compounds. Joyce *et al*. (1968) and Fischer (1971) reported on the relationship between the sensitivity of the chemical senses of a person and the needed dose of drugs to elicit a specific pharmacological effect. Zoeteman *et al*. (1977) therefore concluded that the more sensitive part of the population which assesses water taste as objectionable might also belong to the group most vulnerable to toxic effects.

With the increasing concern with organics in water, Sontheimer (1976) pointed out that water treatment processes that are optimized to lower either the concentration of total dissolved organic materials or the concentration of chlorinated organics will also eliminate taste and odour.

The presence of taste and odour causing compounds in water can also:

1. reduce aesthetic values of rivers and lakes that are used for recreation;
2. contribute to bad taste or toxicity of fish used for human consumption;
3. contribute to high treatment costs for public water supplies by interfering with coagulation, damaging ion exchangers and creating chlorine, carbon and other chemical demands; and
4. tainting certain foods, beverages, and in some cases, destroy the palatability of

drinking water and foods cooked in water.

B. Colour

The decomposition of naturally occurring organic and inorganic matter, as well as industrial wastes, can impart colour to drinking water. The colour is due to the presence of unsaturated organic moieties (chromophores) conjugated in these compounds (Rice *et al.*, 1981). The presence of colour in water supplies, besides being aesthetically displeasing, may (AWWA, 1970):

1. increase chlorine demand;
2. act as a potential algae or bacterial nutrient;
3. foul ion exchange resins in industrial water conditioning systems;
4. interfere with certain coloumetric water analysis;
5. reduce productivity of natural waters by limiting light transmittance;
6. interfere with coagulation processes by chelating metal ions; and
7. increase the concentration and stability of iron, manganese and other metals in water by chelation.

The presence of colour in water may also contribute to its taste. This is well demonstrated in the food industry where colour influences the ability of a person to distinguish the threshold levels of the four basic tastes: sweet, sour, bitter and salty (Maga, 1974). Consumers object to colour on aesthetic grounds and turbidity on the basis that the absence of disease organisms is associated with the absence of turbidity. Freedom from taste and odour requires clarity of water (Schwartz and Moncrieff, 1976).

Pure water should be colourless. The presence of dissolved foreign substances in solution alters colour according to the amount and nature of the material present, and is referred to as "true colour". When water is turbid as well as coloured, the colour is termed "apparent colour". Apparent colour readings are usually higher than true colour values.

The *Guidelines for Canadian Drinking Water Quality* specify a maximun acceptable level of 15 True Colour Units, and less than 15 as an objective (Health and Welfare, Canada, 1978).

Drinking water can also be coloured by algae penetrating plant filters.

Inorganic metallic compounds are common causes of colour in water. A slightly blue or green colour may appear in water distributed through copper pipes when at least 5 mg/L of insoluble copper corrosion products are present in the water (Page, 1973). Dissolved iron (III) chloride can impart a brownish-yellow colour. At levels below 0.3 mg/L of iron and 0.05 mg/L manganese, the red iron stains and black manganese stains are not visible (Buswell, 1928; Griffin, 1960).

The presence of colour is, however, most common in surface water and in shallow wells in limestone regions where solution topography prevails. Studies by Shapiro (1957), Sylvester and Seabloom (1965), and Christman and Ghasseni (1966) demonstrated that the colour in water, originating from the soil, was only an intermediate step in the transformation of organic matter from living or decaying woody tissue, to organic complexes. Christman and Ghasseni (1966) classified colour causing compounds as lignins, flavonoid compounds, and tannins. These compounds are present in the bark and roots of trees and are extractable from the natural environment by water at ordinary temperatures. They further concluded that colour may originate from :

1. the aqueous extraction of living woody substances;
2. the solution of degradation products in decaying wood;
3. the solution of soil organic matter; or
4. a combination of these processes.

Since these compounds arise from the decomposition of plant materials and are carried or transported to a body of water, they are therefore termed "allochthonone", that is, produced elsewhere (AWWA Committee, 1967).

The presence of these natural colour-causing compounds from the decay of aquatic weeds is found to stimulate algal growth (Novak *et al.*, 1975) and further contribute to taste and odour problems. This is in agreement with studies by Pringsheim (1949), Prat (1955) and Shapiro (1957) who obtained similar results with humic compounds.

Du Toit and Page (1930) classified colour causing compounds as:

1. soluble in alkali but not precipitated by acid - fulvic acid;
2. soluble in alkali, precipitated by hydrochloric acid and insoluble in alcohol - humic

acid;

3. soluble in alkali, precipitated by hydrochloric acid and soluble in alcohol - hymatomelanic acid; and
4. insoluble in alcohol -humin

Humus is the total of all the organic compounds in the soil excluding the undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass (Stevensen, 1982).

There have been numerous studies attempting to determine the structure of humus. The complexity of the humus compounds, however, has prevented any conclusive findings. Wilson (1959) determined that fulvic acid is the most water soluble fraction of neutral soil humus and is found in water at higher concentrations than humic or hymatomelanic acid.

In their studies, Dragunov (1961), Christman and Ghasseni (1966), and Kleinhempel (1970) proposed a structure for humus molecules as a huge amorphous mass of polyhetero condensates with certain functional groups protruding from the surface. These functional groups react with chlorine to produce products such as trihalomethane.

A comprehensive review on the structure and chemistry of humus compounds is given by Stevensen (1982).

Croll (1972) found that a large fraction of the TOC in water is often composed of humic substances. Shapiro (1957) and Black and Christman (1963a) concluded that colour causing compounds are resistant to biodegradation. Black and Christman (1963a) also found that :

1. coloured waters have low mineral content;
2. there are no relationships between the ionic content and colour value of waters from different sources;
3. COD did not vary linearly with colour values in water from different sources; and
4. coloured water had very low BOD if organics were from the final stages of microbial decomposition of compounds.

The interest in colour compounds took a different turn in 1974 when Rook (1974) and Bellar *et al*. (1974) studied the formation of trihalomethane in water and agreed that the halogenated organics found were the result of the action of chlorine on naturally

coloured water. Oliver and Thurman (1983) found a good correlation between the trihalomethane formation potential and colour in the water. They determined that colour can be used to predict the trihalomethane potential when most of the organic carbon present was humic materials. In 1976, the National Cancer Institute published a report showing that high doses of chloroform, the most common trihalomethane, could cause cancer in mice. Chlorination and trihalomethane formation are also related to gastrointestinal and urinary tract cancer (Alavanja *et al.*, 1977) as well as other mutagenic effects (Cumming, 1977; Simmon and Tardiff, 1977; Bull, 1983).

Studies by Babcock and Singer (1977) showed that humic acids reacted with chlorine in a much more active way, consuming 75% more chlorine and produced 117% more chloroform per unit of TOC and 23% more chloroform per unit of chlorine than fulvic acids. Gjessing (1976) and Trussel and Umphres (1978), however, questioned the accuracy of these findings based on their water sample sources.

Good particulate removal is important for treating coloured water, since humic substances that cause colour may also be particulate in nature. The removal of humic colour should also reduce the concentration of trihalomethanes that may be formed when the water is chlorinated (McCreary and Snoeyink, 1977). Colour reduction is important for other reasons. For example, Greve and Wit (1971) and Choi and Chen (1976) found that trace organics such as pesticides may be associated with silt and particulate fractions of humic substances. Andelman (1973) also reported the presence of PAH in particulates. Schnitzer and Khan (1972) reviewed the presence of other trace substances that may be associated with humic acids.

Since colour is closely related to taste and odour problems, it should be monitored in any taste and odour studies.

C. The Sources of Tastes and Odours

In the control of taste and odour, it is important to know the causes of the problem. Sources of taste and odour can be placed in two general categories, natural and man-made.

Natural sources include:

1. Biological Causes

a. Aquatic growths such as algae, diatoms, actinomycetes, bacteria, fungi, weeds, and their volatile by-products;

b. Decomposition of organic matter and decaying vegetation such as lignins, protein and carbohydrates, hydrogen sulphide, sulphates and other sulphurous compounds;

c. Disturbance of river banks and bottoms due to high water velocities and scouring action of broken ice; and

d. Stream bottom deposits from anaerobic growth.

2. Chemical Causes

a. Sulphate and hydrogen sulphide from sulphur bearing water;

b. Iron and manganese;

c. Soda ash or alkalinity; and

d. Inorganic salts such as sodium and calcium chlorides.

Man-made sources include:

1. Domestic and municipal sewage effluents;
2. Industrial and manufacturing plant wastes;
3. Chemicals used in water treatment and the by-products formed during treatment processes;
4. Agricultural discharge and feed lot runoff;
5. Drainage of leachate from sanitary landfills;
6. Pesticides, detergents and other chemicals;
7. Decomposition of organic waste;
8. Motor vehicles exhaust residues trapped by ice and snow; and
9. Discharge of storm runoff from urban areas and roadways which may contain hydrocarbons, decomposing organic matter and traces of bituman and tar.

Deicing salt used on highways during winter does not contribute to phenol concentrations or taste and odour problems (Wilford, 1974).

A large variety of odourous substances have been found in drinking water. These compounds may originate from the raw water source; or be formed during treatment, particularly by chlorination. Odour can also be introduced during distribution as a result of microbial growth or release of organic compounds such as aromatic hydrocarbons

(naphthalene) from bitumenous protective coatings (Zoeteman, 1980).

Microbial growths and their metabolic by-products are considered to be the major causes of taste and odour problems in water treatment plants (Sigworth, 1957). Although biological problems are more common, taste and odour originating from man-made sources is more difficult to treat. Zoeteman and Piet (1974) found that odour from unpolluted water was usually of biological origin, while polluted water was relatively independent of biological production processes. Nearly twice as many organic compounds were found in surface water than in groundwater supplies (Zoeteman, 1980).

The chemical properties of phenol and other taste and odour causing compounds have been reviewed by McKee and Wolf in *Water Quality Criteria* (1963), Moncrieff in *The Chemical Senses* (1967), and by Verschueren in *Handbook of Enviornmental Data on Organic Chemicals* (1977).

The commonly used terminology and units of measurement for taste and odour are given in Appendix I.

D. Treatment Methods

There are several alternative methods for reducing taste and odour in water supplies. A complete reduction plan should examine the :

1. prevention of the development of taste and odour causing compounds;
2. prevention of the taste and odour substances already formed from entering the water supply;
3. conversion of taste and odour into non-offensive and safe products; and
4. removal of taste and odour causing compounds.

For the City of Edmonton, method 1 and 2 (prevention) is impractical, at least in the foreseeable future. Method 3 involves chemical oxidation by

a. superchlorination;
b. ozone;
c. chlorine dioxide;
d. potassium permanganate;
e. copper sulphate; and
f. other compounds such as sulfamic acid.

Method 4 involves physical removal by

a. activated carbon, (granular, powdered, and biological);

b. aeration;

c. coagulation; and

d. filtration.

Superchlorination has been used for the control of taste and odour in water treatment plants since 1920 (Cox, 1926; Howard and Thompson, 1926; Wartzl, 1929). Many authors have reported their experience with the use of chlorine in odour control (Calvert, 1940; Riddick, 1951; Harlock and Dowlin, 1958). In his *Handbook of Chlorination*, White (1972) reviewed the history of chlorination and other earlier successes with chlorine. Chlorine is effective in odour control because it is a strong oxidizing agent and an effective disinfectant.

Superchlorination, however, is not always effective for taste and odour removal. In some cases, it can enhance the problem, especially by the formation of chlorophenol, which has an Odour Threshold Unit (OTU) roughly 1,000 times lower than phenol itself (Burtschell *et al.*, 1959). Other chlorinated compounds such as haloforms from humic and fulvic acids, chlorinated anilines and benzenes also have lower OTU's than the unchlorinated compounds (Zoeteman, 1980). The fact that chlorination can result in the formation of trihalomethane (Rook, 1974; Bellar *et al.*, 1974; Coleman *et al.*, 1975) and mutagenic chloramines (Shih and Lederberg, 1976), has further led to the intensified search for a replacement for superchlorination in water treatment.

All the oxidants that can be used in water treatment plants were examined in the comprehensive literature review (Fok, 1984). However, only ozone and chlorine dioxide are being investigated in the present taste and odour control study. Potassium permanganate, although a strong oxidant, has only limited effectiveness in taste and odour control (DuByne, 1963; Erdei, 1963b; Spicher and Skrinde, 1963 Fitzerald, 1966; Popalisky and Pagge, 1972). The application of compounds such as sulfamic acid (Murray, 1970 and 1972); hydrogen peroxide (Raleigh, 1975; Hsi *et al.*, 1977; Gardiner *et al.*, 1983); and copper sulphate (Eredi, 1963a; Lacey, 1976; Ree, 1976) is more limited to specific problems such as the control of algae and bacteria. The only physical method considered was activated carbon, and to a minor extent, coagulation.

The following sections review some of the more recent findings and methods for the use of ozone, chlorine dioxide and activated carbon in taste and odour control.

E. Ozone

Ozone has been used for water treatment in Europe for more than seventy years. The first experiment was carried out by de Merintence in France in 1886 and ozone was used on a full-scale basis at Nice, France in 1906 (Dyachov, 1976). As of 1974, McCarthy and Smith reported over a thousand municipal water treatment plants using ozone as part of their chemical treatment. In most of these installations, however, ozone was used as a disinfecting agent rather than as a means to remove additional organic material.

The use of ozone, compared to chlorine, has not been popular in North America. This reflects a desire to maintain a residual germicidal power in the distribution system, and avoid the higher equipment and operating costs of an ozonation system (Lehr *et al*., 1980). Generally, ozone is more attractive for treating low quality potable supplies when tastes, odours, and colour, are dominant factors for removal. These situations are far more abundant in Western Europe than in North America. Ozone is used more commonly in wastewater treatment and water reuse systems (White, 1978) because of:

1. new pollution control requirements demanding a high degree of wastewater treatment (ozone is known as an excellent water polishing agent);
2. a trend towards wastewater reuse which requires virus inactivation and polishing;
3. the installation of oxygen activated sludge secondary treatment plants;
4. toxicity problems associated with chlorine treatment; and
5. additional benefits of ozone, including a high level of dissolved oxygen in the effluent along with certain types of colour removal and possible reduction in TOC and COD.

In Europe, ozone is used (Miller and Rice, 1978a) for:

1. iron and manganese removal;
2. oxidation of organics, including colour bodies, taste and odour, algae, suspended solids and dissolved solids;
3. microflocculation;
4. bacterial disinfection; and

5. viral inactivation.

Lawrence and Cappelli (1977) found that ozone could destroy sulphates and many surfactants. More recent uses of ozone include increasing the biodegradability of dissolved organics for biological removal in granular activated carbon (Miller *et al.*, 1980; Rice and Browning, 1981).

Chemical Properties

Ozone is a highly reactive allotropic form of atmospheric oxygen. Its formation is endothermic :

$$3/2\ O_2 \rightarrow O_3 \qquad \Delta H = 142\ KJ/mole$$

Ozone is colourless at room temperature and condenses to a dark blue liquid. As a pure liquid or solid, ozone is unstable and explosive. It is poisonous with a characteristic pungent odour, and has a melting point of -193°C, and boiling point of -112°C (Steudal, 1977). Concentrations of ozone in air-oxygen mixtures above 30% are explosive. Explosions may be caused by trace catalysts, organic materials, shocks, electric sparks or sudden changes in temperature or pressure (Kinman, 1972).

The ozone molecule has a dipole moment of 0.5-0.6 debye, forming an obtuse angle of 117° resulting in the delocalized bond formation. The structure of the ozone molecule can be described as resonance hybrid of the four canonical forms (Steudal, 1977; Bailey, 1978):

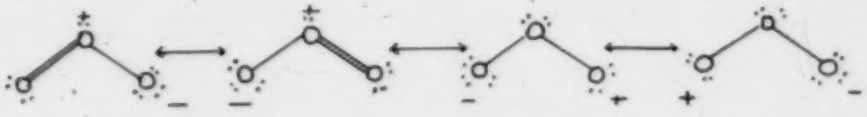

Fig. I. Resonance Structure of Ozone

Ozone is a very powerful oxidant, second only to elemental fluorine among the commercially available oxidants for water treatment. Ozone has an electronegative oxidant potential of -2.07v, referred to the hydrogen electrode at 25°C and unit H-ion activity (Hann and Manley, 1952). On the basis of the resonance description of the ozone molecule, one could predict that ozone should be able to function as a 1,3 dipole (Huisgen, 1963), electrophile (Meinwald, 1955), nucleophile or diradical (Goddard *et al.*, 1973).

Ozone is also extremely corrosive. It completely disintegrates rubber, attacks all plant life but will not react with porcelain or glass. It possibly reacts with PVC, resulting in the loss of ozone (O'Donovan, 1965). A complete list of materials that can be used for ozone contact is given by Damez (1982).

The solubility of ozone in water is a limiting factor that greatly affects ozonation. Theoretically, at 20°C, the solubility of ozone is 570 mg/L (Kinman, 1972). However, because of low partial pressure, the actual reading is 8.92 mg/L (Rice and Browning, 1981). Ozone is unstable in aqueous solution, having an effective half-life of 20-30 minutes in distilled water at 20°C (Rice and Browning, 1981). Ozone decomposition is accelerated by neutral salts and hydroxyl ions and it therefore must be produced on site (Venosa, 1972).

Ozone is more soluble in acetic acid, acetic anhydride, propionic acid, chloroform or carbon tetrachloride than in water (Kinman, 1972).

Chemical Reactions in Water Treatment

There are two major mechanisms by which ozone may react with organic materials: ozonides formation, and ozone decomposition (Hoigne and Bader, 1975).

Ozone oxidizes unsaturated organic compounds through the addition of all three oxygen atoms at the double bond by stereospecific, one step, concerted, 1,3-dipolar cycloaddition (Bailey, 1978) to give ozonides as explained by the Criegee Mechanism (Criegee, 1953; Bailey, 1958 and 1978) (Figure II).

The term "ozonide" should only be used for the 1,2,4-trioxolane structure.

The decomposition of ozone produces free radicals through the following reaction (Morris 1976):

$$O_3 + H_2O \rightarrow HO_3^{\cdot} + OH^-$$

$$HO_3^{\cdot} + OH^- \leftrightarrow 2HO_2^{\cdot}$$

$$O_3 + HO_2^{\cdot} \rightarrow HO^{\cdot} + 2O_2$$

$$HO^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2$$

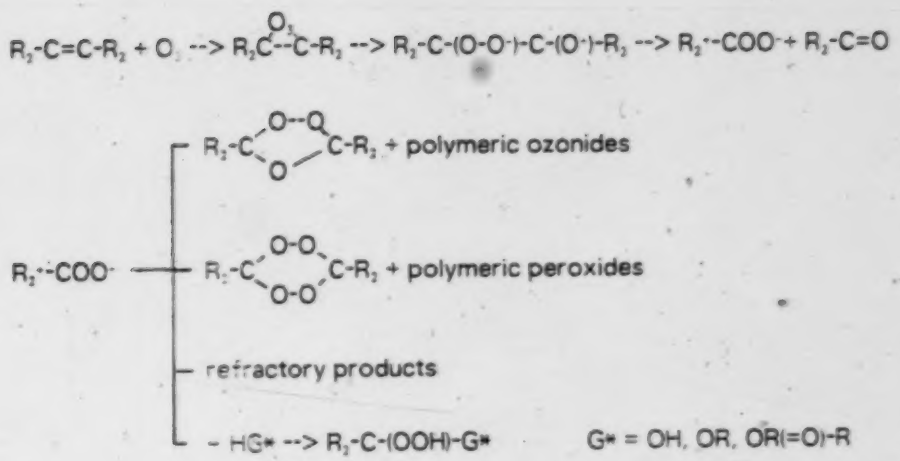
R2-C=C-R2 + O3 --> R2C(O3)-C-R2 --> R2-C-(O-O-)-C-(O-)-R2 --> R2-COO- + R2-C=O
R2-COO-
R2-C(O-O)C-R2 + polymeric ozonides
R2-C(O-O)C-R2 + polymeric peroxides
refractory products
- HG* --> R2-C-(OOH)-G*
G* = OH, OR, OR(=O)-R

Fig. II. Ozone Oxidation: Criegee Mechanism

The free radicals ($HO_2^{\bullet}$ and $HO^{\bullet}$) formed have great oxidizing power and may react with compounds such as metal salts, organic matter, hydrogen, and hydroxide ions present in solution. These radicals are the principal reacting species. The free radical auto-oxidation mechanism may be involved in the disappearance of residual ozone after the initial rapid demand has been satisfied (Morris, 1976).

Among the organic compounds that can be oxidized by ozone are olefinic and acetylenic carbon-carbon double and triple bonds; aromatic, carbocyclic and heterocyclic molecules; carbon-nitrogen and similar unsaturated groups; nucleophilic molecules such as amines, sulfides, sulfoxides, phosphines, phosphiles and arsines; carbon-hydrogen bonds in alcohols, ethers, aldehydes, amines, hydrocarbons; silicon-hydrogen, silicon-silicon and silicon-carbon bonds; and carbon-metal bonds of various types (Evans, 1972). Ozone also attacks most metals except gold and platinum (Kinman, 1972) and reacts with iodides, bromides and chlorides. Ozone will not oxidize ammonia ion in wastewater except when the pH is or remains alkaline (Singer and Zilli, 1975).

Maier (1982) summarized the action of ozone on humus and TOC as follow :

1. Ozonization of organics result in an increase in the polarity. The compounds are more hydrophilic, contain more oxygen atoms in their structure, but have fewer

ethylenic double bonds on the molecules. The remaining molecules have a minor increase in molecular weight and acidic properties as they contain more carbonyl groups which are easier to carboxylate, oxidize, or decompose biologically. Although the adsorption equilibrium on activated carbon is less favourable, the formation capacity of chlorinated compounds is lowered;

2. No significant oxidation of dissolved humus compounds to carbon dioxide occurs; and
3. Ozone concentrations of 0.5 to 1.0 g per gram of TOC are recommended for the treatment of naturally occurring organic compounds.

Ozone behaves as a simple oxidizing agent in many reactions. However, pH, accumulation of reaction products and solvent may alter the predicted reactions in aqueous solution. Ozone may react with activated carbon to form explosive end products (Kinman, 1972), but this is not a hazard in normal water treatment plant practice.

In 1978, Richard and Brener reported that ozone can degrade the pesticides parathion and malathion, to phosphoric acid. Ozone can oxidize ferrous and manganous ions to their insoluble forms, giving either a floc that precipitates or a scum on the water surface (Singer and Zilli, 1975). Ozone interferes with the flocculation process at a concentration of 5.0 mg/L and above (Schalekamp, 1979a). Ozone may also be used to reduce foaming caused by trace organics (Buescher and Ryckman, 1961).

Prengle *et al.* (1975, 1976) studied the reactivity of ozone and defined the "Refractory Index" (RFI) to be the measure of the difficulty of oxidation of a given compound by ozone (Table 1).

Argo *et al.* (1980) found ozone to be effective in removing COD from treated wastewater with no technical limits on COD removal. A COD reduction of 20 mg/L required an ozone dosage of about 75 mg/L, which corresponded to an ozone:COD removal ratio of 3.75.

Table 1. RFI Values for Compounds

Compounds	RFI Value	Qualitative Scale
Potassium cyanide	0.41	Slightly Refractory
Phenol	0.44	RFI<1.0
Chloroform	0.53	
Colour (Pt-units)	0.66	
Complexed Cd-cyanide	0.96	
Pentachlorophenol	1.6	RFI=1-100
Ammonium ion	8	
Simulated medical waste	13	
Glycine	19.7	
Palmitic Acid (NH_4^+ salt)	27.3	
Dichlorobutane	56	
Glycerol	112	RFI=100-1,000
o-Dichlorobenzene	113	Highly Refractory
Polychlorinated Biphenyls	200 (estimated)	
Ethanol	245	
Complexed Ferricyanate	270	
Acetic Acid	>1,000	Very highly refractory

$RFI = Bc^{\circ}t_{1/2} / A_0$
Bc° = ozone supplied to $t_{1/2}$
$t_{1/2}$ = Hours for 1/2 conversion of A_0
A_0 = Initial amount of compound

Ozonation reaction pathways for complicated molecules tend to produce intermediate products that are refractory to further oxidation by ozone. Ozonation, however, can convert non-biodegradable or poorly degradable compounds into forms that readily yield to biological treatment (Rice and Miller, 1977). Guirguis *et al*. (1978) found that ozone pre-treatment can enhance physical-chemical treatment efficiency by reacting with the non-sorbable organics, rendering these compounds more readily sorbable.

Dispite the effectiveness of ozone in the oxidation of compounds such as phenolics, pesticides, detergents and organic matters (Damez, 1976), ozone does not remove trihalomethane (Symons *et al*., 1978).

Richard and Brener (1978) found that ozonation can cause an increase in humic acid concentration and chlorine demand by forming hydroxylated derivatives. Hubbs (1978) found that ozone did not enhance the removal of chloroform precursors in a Louisville water treatment plant. However, his result may have been affected by the presence of a non-ionic surfactants. A similar result, obtained by Symons *et al*. (1977), showed that ozone did not remove trihalomethane and chloroform precursors. Miller *et al*. (1978) found no evidence that ozone oxidizes trihalomethane. Reduction in trihalomethane concentrations upon ozonation appears to occur only by air stripping.

Miller *et al*. (1978) concluded that complete oxidation of dissolved organic materials to carbon dioxide and water in aqueous solution is rare for any oxidant. In general, if an organic material is resistant to oxidation by ozone, the most powerful oxidant used in water treatment, it will also resist oxidation by weaker oxidants.

In order to improve the oxidation of refractories, tests have been conducted using ozone with UV (Prengle and Mauk, 1978), hydrogen peroxide (Nakayama *et al*., 1979), and ultrasound (sonozone) (Dahi and Lund, 1980). UV and hydrogen peroxide used with ozone can convert compounds such as pesticides and acetone to carbon dioxide (Prengle and Mauk, 1978; Nakayama *et al*., 1979). A patented ultraviolet light method was reported to provide some degree of residual ozone in treated water (Collie, 1983). Sonozone can reduce ozone dosage by 57 to 96% and still provide effective disinfection (Dahi and Lund, 1980).

Taste and Odour Control

Ozone can oxidize taste and odour causing compounds (Lowndes, 1971; Kinman, 1975), adding no smell or taste of its own, and improving the appearence of water (Guinvarc'h, 1959; Lowndes, 1971). The most popular deodourizing application involves treatment of sewage plant exhaust gases (Nebel *et al*., 1973a).

The ability of ozone to destroy taste causing phenolic compounds is well documented (White, 1978); ozone has been in use in the City of Whiting, Indiana since 1940.

Ozone counteracts malodourous substances not by masking, but by oxidizing. Although ozone is second to fluorine as an oxidant, it is a superior deodouror. Oxygen is produced as a reduction product of ozone, whereas fluorine reduction products are generally toxic (Nebel and Forde, 1975). Ozone treatment of odourous compounds usually rely on the basic assumption that most odour causing materials are present in low concentrations and are orders of magnitude more odourous than their oxidation products (Bollyky, 1973).

Odoriferous molecules (low Odour Threshold) are all electron-rich. They have functional groups that possess centres of high electron density such as amines, sulphides and unsaturated hydrocarbons (Bailey, 1958). Ozone reacts chemically as if it were electron deficient. Redox reactions occur and oxygen from ozone saturates the excess electron sites of the malodourous substances. The intensity of the odour is therefore reduced by oxidation. An additional benefit is that since substances containing sites of high electron density generally manifest high toxicity, ozone oxidation lowers the degree of toxicity (Nebel and Forde, 1975). Ozone also removes colour by splitting the conjugated double bonds in the compounds (Rice *et al*., 1981). This shifts their light absorption spectrum away from visible wavelengths (Symons, 1976b). Black and Christman (1963b) found ozone to be better than chlorine dioxide for reducing colour in water.

Ozone is effective in oxidizing phenol to oxygenated materials which are non-toxic and biodegradable (Nebel *et al*., 1973b). One of the first stable oxidation products is the biodegradable *cis*- muconic acid. A large ozone dosage will oxidize this derivative to water and carbon dioxide (Eisenhauer, 1971). Other products include catechol, *p*-quinone, fumaric and oxalic acid (Eisenhauer, 1968). Gabovich *et al*., (1969) found

2.3 mg ozone/mg phenol was required for the complete destruction of phenol. Schalekamp (1979a) found 1 mg/L ozone can remove 100 ug/L phenol or 500 ug/L trichlorophenol.

Diaper (1972) found that ozone was effective in eliminating tastes and odours which were accentuated when chlorine was used. Chlorophenolic taste was removed with 1 to 2 mg/L of ozone while destruction of 0.2 mg/L phenol required 1.19 to 1.32 mg/L. An additional benefit of ozone treatment was the aeration effect. Aeration is one of the first method used to reduce taste and odour by removing hydrogen sulphide formed from decomposing organic matters. Aeration also reduced the carbon dioxide content and its corrosiveness. A survey by O'Donavan (1965) found that 0.7 to 1.3 mg/L of ozone reduced the Taste and Odour Thresholds in some treatment plants in West Germany and the U.S. by 100%.

Ozone, however, is not effective in all odour control applications. It will not deodourize acetic acid, ammonia, sulphur dioxide or saturated hydrocarbons.

Application in Water Treatment Plants

Ozone has been sucessfully applied at many water treatment plants for the purpose of taste and odour control. Ozone is commonly used after the application of less expensive methods such as powdered activated carbon and chlorine dibxide fail to produce satisfactory results. There is no documentated case where ozone, properly applied, failed to reduce the taste and odour thresholds in a water treatment plant. The normal dosage ranges from 0.5 to 3.0 mg/L.

In Canada, twenty plants use ozone in water treatment. Of these, nineteen are in Quebec, and one in Manitoba (FACE, 1981).

Ozone is also used by many wastewater and industrial treatment facilities to control air pollution, remove hydrogen sulphides, mercaptans and organic hydrocarbons (Yang, 1975). Some documented successes with ozone can be found in :

Japan : In the control of unpalatable taste and odour at the Chiba Water Treatment Plant in Japan, Sease (1976) found an ozone concentration of 3 mg/L was effective where chlorine levels up to 15 mg/L failed. With 0.5 mg/L ozone, 5.2 minutes of contact

time, and a flow rate of 1.50 L/min, ozonation was able to reduce the Threshold Odour from 40 to 7. Powdered activated carbon was required after ozonation to remove taste and odour causing organisms that might penetrate sand filters. Ozone was transported in stainless steel pipes for 600 m from the generator to the contact tank without any loss.

Michigan : In the treatment of taste and odour in a 69 ML/d system at the City of Monroe, Michigan, LePage (1975) found many valuable secondary benefits from ozonation besides effective taste and odour control. These included improved coagulation and flocculation with alum, partial disinfection, reduced chlorine demands, turbidity reduction and cyanide destruction. The causes of taste and odour had been identified as organics from the river bottom, spring runoff, industrial waste, algae and actinomycetes blooms, and chlorination. The odours had been described as resembling refinery waste and musty smells. If first subjected to chlorination, the odour became more difficult to remove even under improved conditions following pretreatment. LePage found that 1.0 mg/L ozone can reduce the TON of the refinery type odour by 80%, while 4.0 mg/L chlorine, 0.4 mg/L powdered activated carbon, clarification with alum and filtration succeded in reducing the odour value by only fifty percent. A dosage of 1.0 to 1.5 mg/L of ozone successfully removed the musty-earthy odour. No objectionable secondary odour resulted from ozonation except occasionally, a lingering, sweetish ozonish scent due to excessively high ozone doses that left the water supersaturated with oxygen. However, the odour dissipated as the sample reached room temperature. LePage (1981) found that the greater the intensity of taste and odour problems, the more dramatic were the improvements after ozonation. To dramatize the effectiveness of the process, a planned shut-down was carried out eight months after ozonation began. Complaint, absent since ozonation was used, began eleven hours after the shut-down and continued until all distribution mains again contained ozonated water (LePage, 1981).

Quebec City : In Quebec City, ozone is applied at a dose of 1.7 mg/L and at a concentration of 14.0 gm/m^3 of air for treatment of turbidity, colour, and taste and odour.

The process included pre-chlorination, alum coagulation, sedimentation, high-rate gravity filtration and ozonation (Schwartz, 1976). During winter months where the major concern is colour, chemical treatment was by-passed and only filtration and ozonation were used to save operating costs.

Other plants in the Province of Quebec : The effectiveness of ozone in taste and odour control is best exemplified in the use of ozone in a number of plants in the Province of Quebec. Nadeau and Pigeon (1973) found that chlorination produced a much inferior quality of water than ozone in many areas in Quebec. The raw waters contained algae and phenol which produced fishy and "medicinal" tastes. When chlorine was used, the resulting tastes could not be completely removed even by activated carbon. Ozonation not only eliminates the taste and odour, but also disinfects. The chlorination system was retained only for use as a stand-by for security purposes. The operational costs of the ozonation system were nearly the same as the chlorination system.

Winnipeg : The City of Winnipeg has conducted pilot-scale studies to determine the use of ozone to control taste, odour, colour and algae growth in its water supply. Three systems were established:

a. plain filtration followed by ozonation;
b. microstraining with two-stage ozonation; and
c. microstraining followed by chlorination and ozonation.

All three methods were equally effective in lowering TON from about 8 to 2-3 and for suspended organic removal and colour control. The first system gave the greatest flexibility. The capital and operating costs were estimated to be about 50-70% of those for conventional treatment (Summerville and Rempel, 1972).

Ozone is versatile enough to allow its application at various points in the treatment process. Depending on the injection point, ozonation can have many additional benefits.

Increasing the pre-ozonation dosage is effective in controlling algal blooms and their offensive metabolites (Rice *et al.*, 1981), especially when used in conjunction with biological activated carbon (Sontheimer *et al.*, 1978; Heilker, 1979).

Schwartz (1976) also found that many plants had preliminary treatment facilities such as microstrainers and roughing filters to remove algae and similar organic matters prior to ozonation. Although these systems were not completely effective in removing turbidity, the "ozonized floc" produced by ozonation could be removed by downstream filters and the ozonized water could prolong filter runs (Schwartz, 1976). Schwartz and Lancaster (1978) found that ozonation may alter the physical characteristics of colloidal particles, making them more amenable to filtration.

A method called "microflocculation" is being used in the Federal Repulic of Germany to enhance residual turbidity removal. Ozone oxidized organic complexes of iron and manganese forming "micro- floccules" when the complexes were broken (Water Research Centre, 1977). Kuhn *et al.* (1978) reported that the use of ozone with aluminum hydroxide resulted in greater adsorption of humic acid modified during the ozonation process.

Schwartz and Moncrieff (1976) concluded that ozonation preceded by high-rate filtration, with a polyelectrolyte feed system for seasonal application to remove algae and turbidity on filters, was effective for colour removal. However, colour causing organic compounds could be converted to suitable food for bacteria by ozonation. A chlorine residual in treated water to prevent growth of nuisance organisms was recommended (Schwartz and Moncrieff, 1976). These properties and problems of ozonation were observed and demonstrated in water treatment plants in the Federal Republic of Germany (Kuhn *et al.*, 1978). Activated carbon filtration after ozonation, in which the biodegradation can take place is recommended (Kuhn *et al.*, 1978).

Ozone dosages of 1.5 to 4.0 mg/L were reported to remove 15-60 Hazen Colour Units by Boucher (1965) and 45 Units by Campbell (1963). Miller *et al.* (1978a) found ozone to be most effective for taste and odour control and organic

and colour removal if the ozone is applied after a filtration step for the removal of coarse particles and before a second filtration step, either through sand or carbon, to remove the substances acted upon or produced by ozonation. They recommended that ozone should not be used as a terminal step unless the dissolved organic carbon concentration is less than or equal to 0.2 mg/L. Also ammonia cannot be present, otherwise regrowth of nitro-bacteria can occur. The distribution system must be short, with residence time of less than twelve hours, and the finished water temperature must also be low. In Europe, except in rare cases, ozonation cannot be divorced from subsequent chlorine or chlorine dioxide treatment

Mignot (1973) found ozone eliminated taste more effectively than chlorine, chlorine dioxide, or permanganate. Total taste elimination can be achieved by using ozone in combination with powdered activated carbon. In the 1978 AWWA review of disinfection, the Committee acknowledged the ability of ozone to eliminate off-flavours and improve the colour and organoleptic qualities of the treated water. Ozone can destroy phenol equally as well as chlorine dioxide. The Committee believed that when used in combination with chlorine and chlorine dioxide, ozone reacts with HOCl and inhibits the formation of chlorite ion, an undesirable reaction product of chlorine dioxide.

Toxicity

The toxicity of an oxidant in water treatment, is just as important as the compound's effectiveness. Toxicity may originate from the chemical itself, or by forming new and harmful compouds by reacting with unknown pollutants. Some of the toxic factors that should be considered include :

1. excessive dosage or residual;
2. decomposition of the oxidant;
3. by-products formed from reactions with organics in the water; and
4. occupational hazards from the use of the oxidant.

For ozone, the first two factors are not of concern because ozone is unstable in water and the decomposition of ozone only gives oxygen, a desirable product. The major

concern is when the refractory compounds which are formed when ozone reacts with humus and pesticides.

Reaction By-Products

Research by Symons (1976b) has shown that at a disinfection level of less than 5 mg/L, under the conditions tested, ozone will not

1. form trihalomethane;
2. reduce the concentrations of trihalomethane already formed prior to ozonation; and
3. reduce the concentration of trihalomethane precursors as measured by the trihalomethane formation potential (Stevens and Symons, 1977).

Some by-products of ozonation, are:

1. 2-propanol converted to acetone that in turn was oxidized to acetic and oxalic acids with traces of formaldehyde and formic acid (Symons *et al.*, 1977);
2. mutagenic hydroperoxides (Falk and Moyer, 1978);
3. hazardous epoxides and organic peroxides formed by dissociation of ozone (Weil, 1963; Peleg, 1976);
4. mutagenic compounds formed after ozonation of ethanol, benzidine and nitrilotriacetic acid (Simmon *et al.*, 1978);
5. stable heptachlorepoxide from heptachlor (Rice and Browning, 1981);
6. toxic phosgene ($COCl_2$) formed as an intermediate in the ozonation of chlorinated hydrocarbons (Prengle *et al.*, 1976); and
7. toxic metabolities in under-treatment of parathion (Richard and Brener, 1978).

Kinman *et al.* (1978) found ozonated wastewater to be more toxic than unozonated wastewater. However, in comparative toxicity studies of ozonated and chlorinated waters with a defined chemical composition of organic material such as pesticides or detergents, Hartemann *et al.* (1978) found chlorine treated water exhibited a higher toxicity than ozone treated water. The greater toxicity to cell culture systems was speculated to be due to the residual chlorine rather than oxidative products.

Miller *et al.* (1978) determined that since ozone is seldom used as a terminal step in water treatment processes, no adverse health effects could be directly attributed to its use. Although ozone produces many new oxidized moieties and biodegradation products, in general, these are compounds of lesser toxicity, provided sufficient oxidation has

occurred. The exception is when there is the presence of pesticides such as parathion and malathion which form more toxic oxons before degrading upon further oxidation.

Cotruvo *et al*. (1977) analyzed 28 compounds and found only seven indicated some levels of mutagenic activity after ozonation. Nitrogenous compounds seemed to have a greater propensity to produce mutagenic activity after ozonation than did compounds without nitrogen. In two other studies, ozone inactivated the mutagenicity of certain pesticides (dexon and captan); aflatoxin B1; alkylating agents and aromatic amines (Burleson *et al*., 1979; Caufield *et al*., 1979). However, Caufield *et al*. (1979) also found that ozonated dimethylhydrazine produced stable mutagens and that less stable activities resulted from 2-hydroxyethylhydrazine and benzidine. Inactivation was through the saturation of carbon-carbon double bonds. Miller and Miller (1971) had earlier reported the active form of most carcinogens to be an electrophile or carbonium ion. Caufield *et al*. (1979) therefore speculated that the electrophiles or unstable intermediates which decomposed to carbonium ions may be formed by some compounds after ozonation.

The possible cause of hemolytic anemia in Glucose-6-Phosphate Dehydrogenase (G-6-PD) deficient individuals by ozone was studied by Calabrese *et al*. (1977). Dolara *et al*. (1981) found ozonation produced far less mutagenic chemicals than chlorination. Hemolysis, enzyme inhibition, and the decrease in osmotic fragility of erythrocytes can also occur (Freeman *et al*., 1979).

Symons *et al*. (1977) concluded that the toxicity problems are so complex that it is not possible to state if ozone is better or worse than chlorine from the point of view of by-product formation. Legube *et al*. (1981b) agreed, concluding that the beneficial effect of ozone is not necessarily obtained by the ozonation rates needed for disinfection in water treatment.

In summary, the reactions of ozone with organics in drinking water are complex, as would be expected. The results of individual studies may be conflicting because they are heavily influenced by the organics present and oxidizing conditions used. Extreme caution should be used in making general statements. However, it can be stated that the use of ozone is not a panacea for the problem of organics in drinking water.

Trihalomethane Formation

Despite the bleaching and oxidizing power of ozone on other organic compounds, ozone is not very effective in the reduction of trihalomethane concentrations. In their 1978 study, Carns and Stinson found alum coagulation, flocculation and filtration alone could give up to 70% trihalomethane reduction. The addition of ozone before filtration only increased the trihalomethane reduction by 18%. They also found that the presence of bromide in water reduced the effectiveness of ozonation.

Riley *et al*. (1977) expressed concern with the ozonation and post chlorination system which may lead to higher levels of trihalomethane formation than the conventional chlorination process. Oxidation of organic materials with ozone often resulted in the formation of carbonyl compounds (Bailey, 1972) which produce chloroform by reacting with chlorine (Morris, 1975; Dore, 1982). Evidence of enhanced chloroform production in an ozonation-chlorination treatment process has been documented in a EPA pilot plant study (Love *et al*., 1976). The formation of organobrominated compounds due to ozonation is usually very limited (Dore, 1982).

Rice (1980) reviewed the process of ozone and trihalomethane formation. He found that ozone oxidized certain organic compounds completely to carbon dioxide and water at dosage above 100 mg/L ozone and long contact time (more than two hours). He concluded that the best result ozonation can provide is to chemically oxidize some of the trihalomethane precursors to carbon dioxide and the balance to other organic compounds which now cannot produce trihalomethane. However, he also noted that ozone can convert some organic materials into compounds which now can produce trihalomethane upon chlorination.

Riley *et al*. (1977) found pre-ozonation and chloroform production to be extremly pH dependent. When the pH of the system was less than 10, pre-ozonation will result in diminished chloroform production. For a system with pH greater than 10, chloroform production is enhanced by low ozone dosages. For pH greater than 8, even a very high ozone dosage does not reduce the level of chloroform production to less than 30% of a non-ozonated system. The intermediates produced by ozonation of humic acid are relatively stable over twenty-four hour periods with regard to their ability to produce trihalomethane. This phenomenon can be explained by ozone decomposition mechanisms.

since at high pH ozone is more likely to react as a hydroxyl radical rather than as molecular ozone. Therefore, ozone and chlorine at high pH enhanced trihalomethane production less than ozonation at lower pH followed by chlorination at high pH (Hoigne and Bader, 1976).

In a more recent study, Richard and Brener (1980) found ozonation increased trihalomethane formation, especially that of chloroform. The effect of ozone on haloform formation depended upon how ozone was introduced. Ozonated air bubbling produced haloform stripping. Legube *et al.* (1981b) explained the mechanism of the increase in trihalomethane through their studies with aromatics. They found ozonation often resulted in the incomplete degradation of aromatics, and the formation of stable aliphatics with acetyl groups. Post chlorination of these new compounds generally leads to an increase in volatile chlorinated organics production, giving polyhydroxylated compounds as the precursors for haloform reactions. Rice and Browning (1981) found that ozonation of humic materials in water, followed by immediate chlorination, reduced the trihalomethane formation by 65%. However, when ozonized water containing humic acid was allowed to stand for 24 hours and then chlorinated, there was no change in the amounts of trihalomethane formed. Rice and Browning believed that this is an indication that although ozone changed the chemical nature of trihalomethane precursors, there was a continued reaction upon standing to give precursors with trihalomethane formation potential.

Occupational Health

Although ozone decomposes rapidly in water, it has a half-life of five to nineteen hours in the ambient atmosphere (Sease *et al.*, 1973). Continued exposure may result in damage to the lungs, pulmonary congestion and edema (Layton, 1972; Hazucha *et al.*, 1973). Ozone damages cell tissue, impaires enzymic functions and lipid metabolism through its free radical oxidation reaction. Ozone inhalation has also been shown to weaken lung structure, to reduce lysozyme and phagocytic protective activity in the lungs of experimental animals (Hueter and Fritzhand, 1971) and cause chromosome aberrations (Zelac *et al.*, 1971). The mechanisms of cellular injury were explained by Mustafa *et al.* (1980) and Peters *et al.* (1980). Concentrations of 0.02 to 0.05 mg/L are acceptable levels while 0.05 mg/L may result in irritation of the nose and throat (Henschler *et al.*, 1960). A concentration of 0.1 mg/L can results in dryness of upper respiratory mucosa

and 0.2 to 0.5 mg/L causes changes in visual parameters (Lagerwerff, 1963). A level of 1.0 mg/L for longer than thirty minutes may produce headache (Wilsha, 1951).

The Threshold Limit Value (TLV) for industrial workers is 0.1 mg/L or 0.2 mg/m³ (Rapinat, 1982). The maximum concentration for an exposure time of ten minutes is 0.3 ppm according to the ANSI/ASTM Standard.

Canada has adopted a standard exposure time of 0.10 ppm over a one hour period, and 0.03 ppm for a 24-hour period (Erb, 1982). Since people can begin to detect ozone odour at about 0.01 ppm by volume, plant operators can easily leave the area or take corrective action (Kinman, 1972). As a safety procedure, White (1978) suggested continuous monitoring of ambient air in ozone generator rooms, and of hydrocarbons in all mixing chambers and contacting systems. Mixing chambers should be enclosed and excess ozone should be withdrawn and passed through metallic oxide catalytic decomposers to convert the ozone to oxygen. The ozone in the decomposer exit gas should be less than 0.1% by volume.

Ozone released into the ambient air has been shown to destroy nearby plants and shrubbery (Bean, 1959).

Safety procedures for plants using ozone were reviewed by Damez and Vigouret (1980).

With proper monitoring and control, ozone should present no occupational health problem when used in a water treatment plant.

Conclusion

Ozone is the strongest oxidizing agent that can be used in water treatment plants. If ozone fails to react with any chemical, it is safe to assume that other oxidants, such as chlorine dioxide, will also be ineffective. When properly employed, ozone is effective in the oxidation and elimination of many taste and odour causing compounds.

Although there are many questions regarding the safety of ozone and by-products formation, the proven benefits of ozonation cannot be ignored. The science of ozone generation is well developed allowing for its safe and successful application in water treatment plants. The only disadvantage is the higher capital and operational cost, a question on which the consumer must decide.

F. Chlorine Dioxide

Chlorine dioxide was first used as a water treatment process in the United States at Niagara Falls, New York, in 1944 (Synan *et al.*, 1944; Synan *et al.*, 1945; Aston, 1947), for the treatment of phenolic taste and odour as a result of water pollution from industries, algae and decayed vegetation. A survey by Granstrom and Lee in 1958 found fifty-six plants in the U.S. using chlorine dioxide for the control of phenolic or algae-related taste and odour. Chlorine dioxide is also used extensively in the pulp bleaching, textile and food industries (Gall, 1978). As of 1978, 495 water treatment plants in Europe, 84 plants in the U.S., and ten plants in Canada used chlorine dioxide (Miller *et al.*, 1978). The Canadian plants all located in Ontario, use chlorine dioxide to remove taste and odour caused by phenolic substances.

The popularity of chlorine dioxide is due mainly to its versatility. Chlorine dioxide is more commonly used in Europe as a final disinfectant or to provide a residual for finished water than for pre-treatment purposes as is frequently practiced in America. European plants have reported that chlorine dioxide provides a longer-lasting oxidant residual than chlorine. Accordingly, they add a lower concentration of chlorine dioxide, 0.1 to 0.5 mg/L, than the U.S. plants. Chlorine dioxide can be used for taste and odour control, colour removal, iron and manganese oxidation, organics oxidation, disinfection and for providing a lasting residual in the distribution systems (Miller *et al.*, 1978).

Knoppert *et al.* (1980) reviewed water treatment practices in Europe, and concluded that chlorine dioxide and ozone can be considered the only practical alternatives for the replacement of chlorine as a strong disinfectant-oxidant. Chlorine dioxide can be used instead of chlorine for pre-chlorination and for ultimate safety disinfection. Ozone can be considered as a substitute for the primary disinfectant.

Chemical Properties

Chlorine dioxide has a molecular weight of 67.5 grams per mole, comprised of 53% chlorine and 47% oxygen by weight. It is a greenish-yellow to red gas, depending on its concentration. It has a distinctive odour similar to chlorine, but more irritating and toxic. The odour is evident at 14-17 ppm in air, and at 45 ppm it is irritating (White, 1978). The gas is soluble in water at room temperature to the extent of 2.9 grams of chlorine dioxide

per litre at 30 mm Hg partial pressure (White, 1972). In alkaline solution, disproportionation to chlorite and chlorate ions occurs (Steudel, 1977):

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + H_2O + ClO_3^-$$

The chlorine dioxide molecule has angular $\angle OClO$ of 117.5° with a bond order of about 1.5 A° based on a resonance structure of the AB_2 type (Steudal, 1977) (Figure III).

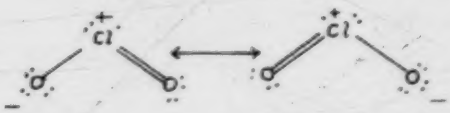

Figure III. Resonance Structure of Chlorine Dioxide

Chlorine dioxide can be compressed to a liquid with a density of 2.4, boiling point of 11°C and melting point of -59°C (Sconce, 1962). In gaseous form, chlorine dioxide is very explosive. Explosions can be brought on by a rise in temperature; exposure to light, shocks, electrical discharge, or allowing the gas to come into contact with organic substances such as rubber and cork, or inorganic mercury and sulphur (Masschelein and Rice, 1979). This tendency to explode at the slightest change in environment is even greater in the compressed liquid state (White, 1972). Ward (1976a) found that chlorine dioxide gas can be safely handled only if its concentration in air does not exceed ten percent. Steudal (1977) recommended that chlorine dioxide be handled as the pyridine adduct $C_5H_5N.ClO_2$, or after dilution in carbon dioxide. In the pulp and paper industry, which requires high concentrations of the gas in solution, chlorine dioxide is usually diluted with air or nitrogen (Sussman and Rauh, 1978). Exposure of the gas to light results in photochemical decomposition to chlorine heptoxide (Cl_2O_7), chlorinemonoxide (ClO), chlorine, and possibly oxygen (Booth and Bowen, 1925).

Chlorine dioxide dissolves in water at neutral pH with almost no hydrolysis (Masschelein, 1979). Chlorine dioxide is more soluble in water than is chlorine, and the solubility is temperature dependent. At 20°C and 40 mm Hg partial pressure, the solubility in water is 4.0 gm/L (Sconce, 1962). In water, chlorine dioxide is entirely harmless (White, 1972). It does not react chemically with water and can be easily expelled by blowing a small amount of air through the solution. Photodecomposition of the aqueous

solution occurs as a function of both time and intensity of ultraviolet light to give chloric and hydrochloric acid (Bowen and Cheung, 1932). An aqueous solution of chlorine dioxide can retain its strength for serveral months if it is properly stored in the dark.

Theoretically, chlorine dioxide has about 2.5 times the oxidizing power of chlorine when it changes from the +IV valence state to the -I (chloride) state (Ward, 1976b):

for chlorine dioxide -

$ClO_2(+IV) + 5e^- = Cl^- + 2O^{2-}$

$5 \times 35.5 \times 100 / 67.5 = 263\%$

for chlorine

$Cl_2(0) + H_2O \rightarrow HOCl + HCl + 2e^-$

$2 \times 35.5 \times 100 / 71 = 100\%$

This oxidizing capacity, however, may not be used fully, since chlorine dioxide reacts with many substances in water to give chlorite ions:

$ClO_2 + e^- \rightarrow ClO_2^-$

with second step oxidation by chorites,

$ClO_2^- + 4e^- + 4H^+ \rightarrow 2H_2O + Cl^-$

The full oxidation potential of 1.15 volts (Feuss, 1964a) is released when chlorine dioxide undergoes five valence changes in reactions with phenol or other compounds (White, 1978).

When chlorine dioxide reacts with electron-rich odour causing compounds, such as amines, it tends to gain only one electron, forming the stable chlorite ion. This means that only one-fifth of the potential oxidizing power is utilized. As the pH decreases, chlorite becomes less stable, and more available for reaction, but the amines are more protonated, and less reactive (Rosenblatt, 1978).

Chemical Reactions in Water Treatment

The reactions of chlorine dioxide have been investigated by many researchers. White (1978) summarized the following properties of chlorine dioxide in water treatment:

1. although extremly soluble in water, chlorine dioxide does not react chemically with water, and it does not dissociate or disproportionate as do chlorine solutions;

2. chlorine dioxide reacts rapidly with oxidizable material without reacting with the ammonia nitrogen present;
3. between pH 5 and 9, an average of 5.2 parts by weight chlorine dioxide oxidizes one part by weight of the sulphide ion instantaneously and in one step to sulphate ion, avoiding the formation of colloidal sulphur (Ward, 1976a);
4. when used as a pre-treatment chemical in potable water supplies, it does not contribute to the formation of chloroform (Symons, 1976b);
5. it displays a "chlorine dioxide demand" as does chlorine, but because of its potentially greater oxidizing power, it displays a proportionally higher demand than chlorine in the same environment;
6. the predominant reaction in water or wastewater treatment is the reduction of chlorine dioxide to chlorite ion. Since this may be toxic to man or aquatic life, it is of considerable interest that the application of chlorine dioxide followed by ozonation may prevent the formation of chlorite ion. The compatibility of ozone and chlorine dioxide, however, is not known;
7. it is specific for the destruction of phenols; and
8. it displays some bleaching effect upon the organic colour in water.

Ward (1976b) outlined some of the reactions of chlorine dioxide with some of the commonly found constituents in water and wastewater. These reactions include: oxidation of sulphides to sulphate ion; destruction of cyanide with cyanogen chloride formation; oxidation of ferrous and soluble manganese to ferric and insoluble manganese; and oxidation of secondary and tertiary amines, mercaptans, organic sulphides and disulphides. Phenol and chlorophenols will also be oxidized to low molecular weight, non-aromatic carboxylic acids.

Some of the non-reactive compounds include ammonia salts, alkanes, alkenes, alcohols, glycols, diols, aldehydes, ketones, esters, acids, primary amines and unsubstituted aromatics (Ward, 1976b). Many of these compounds may react with chlorine, creating a higher "chlorine demand". ABS type detergents also resist chlorine dioxide in water treatment (Masschelein, 1979). Benzoic acid, phenylsulphonic acid, thiazines and cinnamic acid do not react with chlorine dioxide. The first two are oxidized by ozone, but the reactivity of the last two with ozone is not known (Miller *et al.*, 1978).

One of the great advantage of chlorine dioxide is that it does not react with ammonia to give chloramines (Rosenblatt, 1978). Chlorine dioxide can also remove many pesticides such as methoxychlor, aldrin and parathion (Masschelein, 1979). In their 1971 study, Gomaa and Faust found chlorine dioxide to be the oxidant of choice for removing dipyridylium quaternary herbicides from water.

In comparing ozone with chlorine dioxide, Rosenblatt (1978) and Miller *et al.* (1978) listed these differences between the oxidants in water treatment:

1. ozone decomposes rapidly and spontaneously in neutral aqueous solution, whereas chlorine dioxide is quite stable and can maintain a residual longer than an equivalent chlorine concentration;
2. ozone is extremly reactive and can lower TOC, COD and BOD dramatically. Chlorine dioxide has a considerably lower redox potential and is highly selective in its chemical reactions;
3. in its reaction with organic compounds, the part of the ozone molecule remaining after the reaction is harmless or even desirable (oxygen). Chlorine dioxide reaction may leave behind chlorite ion or other chlorine-containing inorganic species;
4. ozone disinfection abilities can be interfered with by high organic loadings, whereas highly selective chlorine dioxide may maintain its residual and reactive potential;
5. ozone will oxidize some materials that chlorine dioxide will not oxidize, such as primary and secondary amines, amino-acids, double bonds conjugated with carbonyl groups; and
6. oxidation products formed by ozonation do not contain halogen atoms, unless bromide ion is present. In this case, bromide is oxidized to bromine which then may react with organic materials present. Chlorine dioxide oxidation generally does not result in adding halogen atoms.

The reactions of chlorine, chlorine dioxide and ozone were summarized by Miller *et al.* (1978) and are presented in Appendix II.

Taste and Odour Control

Chlorine dioxide has been used for the treatment of taste and odour in many areas of the U.S. In 1947, Aston (1947) found chlorine dioxide could successfully assist chlorine in the control of tastes resulting from raw water being contaminated with phenolic substances and algae. White (1972) listed four reasons why chlorine dioxide is the chemical of choice when dealing with taste and odour arising from phenolic compounds:

1. chlorine dioxide will not react with ammonia or nitrogenous compounds, including the simple amino-acids, as will chlorine;
2. chlorine dioxide reacts completely to destroy the taste-producing phenolic compounds many times faster than free available chlorine. This is a result of its oxidizing capacity being twice that of HOCl;
3. chlorine dioxide will destroy any chlorophenol taste caused by pre-chorination; and
4. the efficiency of chlorine dioxide is not impaired by high pH.

Earlier studies by Synan *et al*. (1944), McCarthy (1945), Mounsey and Hager (1946), found chlorine dioxide to be most effective when applied as a post-treatment process following pre-chlorination. Chlorination of phenol results in the formation of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4,4-dichloroquinone and 2,6-dichlorophenol. All of these compounds contribute to the intensity of taste and odour. Further oxidation by more powerful chlorine dioxide will render these compounds tasteless. The mechanism of phenolic compound destruction was explained by Adams (1931), Faber (1947) and Burtschell *et al*. (1959).

Glabisz (1966) reported that 1.0-1.7 grams of chlorine dioxide per gram of phenol with a contact time of 15 minutes was sufficient to remove phenolic taste. Conventional treatment doses between 0.15 and 0.25 mg/L usually are sufficient to guarantee suitable organoleptic properties (Masschelein, 1979). Buydens (1970) found phenol was nearly completely removed when chlorine dioxide was added before the clarification/flocculation step in water treatment processes.

The higher volatility of chlorine dioxide in aqueous solution make it most desirable in odour control of foul air associated with wastewater treatment and certain odouriferous processes which contribute to air pollution (White, 1978).

Application in Water Treatment Plants

Although chlorine dioxide is not as effective as ozone in terms of oxidizing power, there have been many successes with the use of chlorine dioxide in taste and odour control.

In their 1958 survey of the 52 plants using chlorine dioxide for taste and odour control, Granstrom and Lee found that fifteen applied chlorine dioxide to raw water; three after coagulation; six after settling; and thirty-five after filtration. In some regions in Europe, chlorine dioxide was used regularly with chlorine, ozone, and activated carbon for the control of taste and odour. It has proven to be very effective, especially when used with ozone (White, 1978).

Taste and odour control is the major reason the Hamilton, Ohio plant uses chlorine dioxide for disinfection. Originally, the plant used chlorination to give acceptable bacterial levels but maintained a low chlorine residual. When the chlorine residual was increased according to regulation, it resulted in complaints of taste and odour proportionate to fluctuation in chlorine addition. The use of chlorine dioxide provided satisfactory water, meeting consumer and government standards. Although chlorine dioxide costs approximately 50% more than chlorination, Augenstein (1974) found that it was justified by consumer satisfaction and that chlorination equipment was no longer required at distant booster stations.

Other tests conducted by Cardey (1953) found that chlorine dioxide destroyed phenol, did not form chlorinated phenols, and that the oxidant functioned equally well in acidic or basic solutions. A reaction time of fifteen minutes destroyed 100 to 130 mg/L of phenol, causing a drop in final pH to 2 to 4, attributed to the formation of organic acids.

The use of chlorine dioxide is not limited to taste and odour control.

Miltner (1976a) indicated that chlorine dioxide reacts with natural humic acid and effectively reduces colour in drinking water supplies.

Toxicity

Although chlorine dioxide at 100 mg/L increases mortality in rats (Haller and Northgraves, 1955), it is considered safe at concentrations used in water treatment processes. However, at a higher concentration (9 mg/Kg body weight) chlorine dioxide can act as an antithyroid agent (Bull, 1983).

The major concern with the use of chlorine dioxide is the unknown properties of chlorite. Despite many studies, the effects of chlorite remain unclear. The general consensus appears to be that chlorine dioxide or chlorite show no harmful effect at concentration levels used in water treatment processes.

Calabrese *et al.*, (1978), Bull (1980), and Greenberg (1981), however, reviewed various disinfectants and concluded that there were many unanswered questions concerning the toxicity of chlorine dioxide, and that there was insufficient evidence to accept chlorine dioxide as a replacement for chlorine as the prime disinfectant.

The formation of chlorite is discussed in detail in the next section.

Chlorite Formation

Abdel-Rahman *et al.* (1980a) reported that chlorine dioxide may form chlorite (ClO_2^-), chlorate (ClO_3^-) and chloride (Cl^-) as end products. In potable water treatment systems, Montiel (1976) found that chlorine dioxide dosages of 1.3-4.0 mg/L gave, after three days at 25°C, 50% chlorine dioxide, 25% chlorite, 9% chlorate and 14% chloride with 2% analytical error. In the Paris water supply, 2 mg/L chlorine dioxide gave a chlorine dioxide residual of 0.125 to 0.25 mg/L chlorite after 48 hours (Montiel, 1976). This showed the superior residual power of chlorine dioxide, compared with chlorine. Conversely, Myhrstad and Samdal (1969) found that chlorine dioxide was completely converted to chlorite within 35 minutes in water from a system using microstraining and ozonation for treatment.

The chlorite ion residual is of special concern because it reacts with hemoglobin to form methemoglobin (Miltner, 1976b; Musil *et al.*, 1963) and ruptures red blood cells (Richardson, 1937). Heubner and Jung (1941) and Bodansky (1951) also demonstrated similar undesirable properties with chlorate but at a much slower rate. Abdel-Rahman *et al.* (1980b) reported that chlorite induced a decrease in glutathione, a tripeptide important in cellular respiration, *in vivo*. Glutathione acted in a protective capacity by being more

readily oxidized than vital cellular constituents and played an important role in maintaining hydrogen peroxide levels in the body system (Keller, 1971).

It has been postulated that if the chlorine dioxide solution generated is pure, the formation of chlorite is likely to be at a minimum, and chloride at a maximum (White, 1978). In the presence of excess chlorine (or another strong oxidant), chlorite can be reoxidized to chlorine dioxide (Love *et al.*, 1976; Miller *et al.*, 1978).

Symons *et al.* (1977) and Masschelein (1979) pointed out that with a LD_{50} (rats) for chlorite and sodium chlorite to be at 140 (Musil *et al.*, 1963) and 182 mg/Kg (Sperling *et al.*, 1959), respectively, if all the chlorine dioxide gave rise to chlorite, this corresponded to 105 mg chlorine dioxide per kg. They therefore concluded that there is no hazard with conventional doses. Extensive study by Abdel-Rahman *et al.* (1980b) found daily dosages of up to 1,000 ppm of chlorine dioxide, chlorate, and chlorite produced no methemoglobin in rats after two months. Changes in erythrocytes morphology, however, were observed.

In his review, Bull (1980) found the human health effects of oxidation products of chlorine dioxide to be unknown, although in preliminary studies on mice, there was no evidence of increased incidence of skin tumors. Bull found that at a concentration not clearly established, but possibly within the range that might be used for disinfection, chlorite can produce hemolytic anemia. A community using chlorine dioxide for disinfection and taste and odour control with a chlorite ion concentration of 5 mg/L showed no hematological symptoms. Bulls' data, however, did not include tests for subclinical hemolytic effects. Bull (1980) and Greenberg (1981) were interested in the decrease in hemoglobin and hematocit in an individual deficient in glucose-6-phosphate dehydrogenase (G-6-PD). Thirteen percent of Black males in the U.S. and 60% of Kurdish Jews showed this enzyme deficiency (Keller, 1971). G-6-PD is probably the single most prevalent hereditary enzymatic defect of clinical significance (Beutler, 1967). Lubbers *et al.* (1983), however, found no detrimental effects in healthy individuals and G-6-PD deficient subjects with the oral ingestion of 5 mg/L of chlorine dioxide. The importance and physiology of G-6-PD deficiency and methemoglobin reduction was explained by Keller (1971).

Reversible oxidation of hemoglobin to methemoglobin occurs when erythrocytes are exposed to mild oxidation. Further oxidation stress may result in the oxidation of sulfydryl (-SH) groups of globin, causing irreversible damage with the formation of mixed disulfides between glutathione and hemoglobin (sulfhemoglobin). Hemolysis will occur when hemoglobin is denatured to give Heinz Bodies (Keller, 1971). The sensitivity of an individual's hematopoieic system to oxidation stress to produce hemolytic anemia is variable. It is more common in patients undergoing long-term hemodialysis and in newborn infants (Goldstein *et al.*, 1974). G-6-PD deficient individuals are also more vulnerable to oxidation hemolysis (Keller, 1971; Calabrese *et al.*, 1977).

Using tracer chlorine (^{36}Cl), Bull (1980) tested the effect of chlorine dioxide in the body systems. The half-life of ^{36}Cl derived from $^{36}ClO_2$ in plasma of rats is approximately 44 hours (Abdel-Rahman *et al.*, 1980b). Only 40% of the total dose of chlorine dioxide is eliminated in 72 hours. Bull found that some ^{36}Cl is fixed in tissue macromolecules. This may be an indication of carcinogenic or mutagenic potential.

In his study of long-term chronic administration of chlorine dioxide in drinking water to rats, Haag (1949) found that 10 mg/L over a two year period showed no discernable toxic effects. Enger (1960), however, reported that consuming 0.7 mg/L chlorine dioxide resulted in a feeling of weakness and gastrointestinal troubles in laboratory workers. Musil *et al.* (1963) attributed the symptoms to:

1. chlorine dioxide itself;
2. the final products from the reactions between chlorine dioxide and substances in the water; or
3. unreacted chlorite from the generation of the chlorine dioxide.

Hopf (1967) proposed that the toxicity of chlorite might be approximately the same as chlorate and reported symptoms of a "weak furry feeling" on the tongues of subjects who drank sodium chlorite solutions at concentrations greater than 0.3 mg/L.

Tardiff and Bercz (1977) reported that there was no statistical deviation from normal hemoglobin, hematocrit, red cell counts, reticulocyte, methemoglobin or osmotic fragility values for monkeys exposed to 20 to 200 mg/L chlorine dioxide for 13 weeks. Other hematological parameters: Heinz Bodies, differential counts, red cell and leukocyte morphology, serum bilirubin and enzyme levels also were within normal limits, indicating a

stable homeostatic response (Tardiff and Bercz, 1977).

Reaction By-Products

Although chlorine dioxide is commonly used to eliminate phenolic compounds, chlorination of phenol can occur. Stevens *et al*. (1978) found that the reaction of chlorine dioxide with phenol can cause chlorine substitution, ring cleavage, or both, depending on the phenol, and the conditions of the reaction. The chlorinated products generally have different structures and are either less odourous or are formed in much lower yield than those formed when chlorine is applied. Glabisz (1968) found that at a chlorine dioxide concentrations of 1 mg/L and above, the reaction products of phenol fell into two groups. In the first group, the ring structure is retained and the end products are quinones. This group consisted of *para*-dihydric and monohydric phenols that are not *para*-substituted. The second group is characterized by phenol which undergoes ring cleavage to give carboxylic acids products. This included *para*-alkyl, *ortho*-, or *meta*- dihydric phenols. Although chlorine dioxide tended to favour oxidation over chlorination, the relative amount of chorinated versus oxidized products depended on the relative amounts of both chlorine dioxide and phenols present. Excess chlorine dioxide tended to favour oxidation.

The amount of chlorinated products formed depends on the amount of chlorine dioxide residual maintained, and the concentration and nature of the organic materials present in the water. Some of the non-chlorinated products of chlorine dioxide oxidation, like quinones and epoxides are of questionable safety and unknown toxicological significance. Thorough testing of the reaction products is recommended (Stevens *et al*., 1978). However, Lykins and DeMarco (1983) found that chlorine dioxide produced no organic byproducts other than those noted with chlorine disinfection.

Tests carried out at the U.S. EPA Water Supply Research Division Laboratory found an increase in C2 through C8 aldehydes after treatment of natural water with chlorine dioxide (Stevens *et al*., 1978). Some of the reactions of chlorine dioxide with organic and inorganic materials were reviewed by Stevens *et al*. (1978).

Trihalomethane Formation

The effect of chlorine dioxide on trihalomethanes is similar to that of ozone: it has little effect on the trihalomethane concentration.

Mallevialle (1975) found that humic materials treated with pure chlorine dioxide (containing no free chlorine) did not form trihalomethanes. This finding was confirmed by Love *et al*. (1976) and Miltner (1976a). The later author also found that chlorine dioxide plus excessive chlorine caused formation of lower concentrations of trihalomethanes than the same amount of chlorine alone.

Vilagines *et al*. (1977) compared the use of chlorine dioxide and sodium hypochlorite as terminal treatment steps and examined their ability to produce trihalomethanes. Results showed that trihalomethane production occurred only with hypochlorite and not with chlorine dioxide. When excess chlorine was used with chlorine dioxide, trihalomethane formation occured.

In a 1980 review of European water treatment plants, Knoppert *et al*. found that chlorine was preferred to chlorine dioxide for post disinfection. This was because of the possible health risks associated with the use of chlorine dioxide, and the considerable reduction in trihalomethane precursors obtained by other treatment methods.

Occupational Health

There is considerable disagreement concerning the occupational hazards of chlorine dioxide (Haller and Northgraves, 1955). Most reports are concerned with exposure in air, especially in the pulp and paper industry. They describe symptoms of local contact irritation and two cases of illness, including one fatality from exposure to 19 ppm inside a bleach tank (Elkins, 1959; Symons *et al*., 1977). The Threshold Limit Value (TLV) for industrial inhalation exposure is 0.1 ppm (Rosenblatt, 1978).

In their survey, Miller *et al*. (1978) found that many plant operators were concerned with the potential explosiveness of sodium chlorite when not handled and stored properly. Sussman and Rauh (1978) believed the claim was unfounded because sodium chlorite was no more hazardous than any other oxidizing agents. However, problems can arise from the mixing of sodium chlorite, as a solid or a strong solutions, with acids. Under these conditions, large amounts of chlorine dioxide may be evolved unexpectedly. Problems may also occur from the contamination of the solid with

combustable organic material or reducing agents, capable of causing a fire.

Recommended Dosage

Musil *et al*. (1963) asserted that chlorite ion, as an oxidizing agent, caused the oxidation of hemoglobin to methemoglobin *in vivo*. He suggested a zero concentration of chlorite because of the hazard of methemoglobinemia in nursing babies. Based on these observations, the Norwegian Health authority recommended removing chlorite from drinking water. In West Germany, the maximum applied dose of chlorine dioxide is limited to 0.3 mg/L because of the presumed health effects. In the Soviet Union, it was concluded that organoleptic deterioration rather than health considerations should limit the concentration to 0.4 to 0.45 mg/L (Calabrese *et al*., 1978; Greenberg, 1981). The National Academy of Sciences (1980) reported that chlorine dioxide concentrations above 10 mg/L contained chlorite which had a deleterious effect on red blood cells. The U.S. EPA, therefore, recommended that residual oxidants attributed to chlorine dioxide (ClO_2, ClO_2^-, ClO_3^-), be kept below 0.5 mg/L to prevent potential adverse effects on sensitive individuals and children (Vogt, 1980). The maximum residual concentration releasing no objectionable taste and odour is described as 0.4 to 0.5 mg/L (Masschelein, 1979).

Conclusion

The effectiveness of chlorine dioxide for removing phenolic taste and odour is well documented. Although chlorine dioxide may be slightly more expensive than chlorine, its stronger oxidizing power and residual effect may outweigh the difference.

Since chlorine dioxide is not as powerful as ozone, pilot studies should be carried out to evaluate the two oxidants effectiveness in eliminating taste and odour problems. The toxicity problem of chlorine dioxide and chlorite ion is not completely resolved and should be taken into careful consideration. The choice between chlorine dioxide and ozone will depend on the need and the economic picture.

G. Activated Carbon

The deodourizing and decolourizing properties of activated carbon was first recognized in 1792 (Mantell, 1928). *Engineering* reported its use for municipal water supplies in London in 1866. Powdered activated carbon was used to remove taste and odour from water as early as 1930. In many instances, it was recognized as the only known means of removing objectionable taste and odour to produce palatable water (Baylis, 1935). Activated carbon continued to play an important part in water treatment, and in 1978, the US Environmental Protection Agency (1978a) proposed a resolution specifying the use of granular activated carbon in the treatment process to control the synthetic organic chemicals in drinking water supplies. This proposal met with critism (AWWA, 1978b; Pendygraft *et al.*, 1979a) and was subsequently dropped. However, interest in activated carbon for the control of organics in water remains high.

Activated carbon is employed widely in the beverage, food, and drink industries for removing taste, odour, and other organic components generally classified under the "TOC" label (Slejko and Meigs, 1980).

Activated carbon physically removes organic compounds from water. Oxidation, on the other hand, may change the detectable taste and odour values, but the new, sometimes tasteless compounds are allowed to pass through the system. Borneff (1980) found that activated carbon treatment can improve drinking water quality by eliminating organic chlorine components, polycyclic aromatic hydrocarbons (PAH), and nitrosamines. At present, no known treatment methods can eliminate all toxic substances, but activated carbon has the greatest efficiency for removing taste and odour causing compounds and most toxic compounds, to below detection limits.

Adsorption Mechanism

Activated carbon removes taste and odour from water by the process of adsorption. The vast surface area of the carbon allows for the adsorption of many nonpolar compounds. Cheremisinoff and Morresi (1978) reported that the adsorption power of activated carbon depended upon the:

1. physical and chemical characteristics of the adsorbent (surface area, pore size, and chemical composition);

2. physical and chemical characteristics of the adsorbate (molecular size, molecular polarity and chemical composition);
3. concentration of the adsorbate in the liquid phase (solution);
4. characteristics of the liquid phase (pH and temperature); and
5. residence time of the system.

Properties of Activated Carbon

The source and method of preparing carbon are important factors when determining its suitability for a given application.

Activated carbon can be made from a variety of materials including peat, bituminous coal, lignin, pulp mill black ash, bagasse and bones (Hassler, 1963; Snoeyink, 1976). Better grades of granular carbon are prepared from coal, lignite, nut shells, and petroleum residue, while powdered carbon is usually prepared from wood and sawdust. The activation of carbon consists of burning off the amorphous decomposition products and enlarging the pores in the carbonized materials. The carbon is then dried and heated to 180 to 270°C with the evolution of carbon monoxide, carbon dioxide, and acetic acid. Complete carbonization is obtained at a temperature of 400-600°C. Activation by carbon monoxide or steam at 750 to 950°C will burn off decomposition products, and expose and widen the pores in the development of a macroporous structure (Ford, 1981).

Carbon is graded by its phenol value[2] and iodine number[3]. Most commercial carbons have a phenol value of 15 to 30 (Rosen and Booth, 1971). Standards for testing and grading GAC and PAC have been given by AWWA (1974 and 1978a, respectively). Typical commercial grain sizes for GAC are 8x30, 12x40 or 20x40 US standard mesh [4]. PAC is generally considered to consist of particles of less than 150 mesh size (0.1 mm diameter). It is usually pulverized so that 95 to 100% will pass a 100 mesh sieve (149 micrometers nominal opening) and between 50 to 90% will pass a 325 mesh sieve (Fornwalt and Hutchins, 1966). Granular bituminous coal is heavier and has larger surface

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[2]Phenol value is the amount of carbon, expressed in parts per million, required to reduce a standard phenol concentration of 100 ppb to 10 ppb.
[3]Iodine number : the milligrams of iodine adsorbed by 1 gram of carbon when the iodine concentration of the residual filtrate is 0.02 N.
[4]20x40 carbon is comprised of particles that will pass through a US Standard Mesh Size No. 20 screen (0.03 in) but would be retained on a US Standard Mesh Size No. 40 screen (0.017 in) (Benefield *et al.*, 1982).

area than lignite carbon. The PAC by comparison is heavier and has a smaller surface area (Snoeyink, 1976).

Activated carbons differ in their effective size, uniformity coefficient, hardness and apparent density. Badorek *et al*. (1980) tested fifteen types of adsorbents including products from bituminous and lignite coals, petroleum by-products, peat and resin. They found that adsorbents that were optimized to remove trihalomethane displayed much lower TOC removal than the more typical grades of activated carbon because of insufficient numbers of pores in the larger size range.

Fiessinger and Brener (1980) tested twelve different types of granular activated carbon, and found most carbons have similar adsorption capacity for taste and odour and general organic removal. The main differences were in the physical characteristics, and price. Generally, a high iodine number together with a high molasses (or methylene blue) number[5] is beneficial.

Sontheimer (1979b) found that the grades of carbon used for taste and odour removal must have good phenol values, but were not required to have high activity for other substances. Therefore the carbon could have only small pores and a smaller surface area. For the extra benefit of removing organics, a new and more expensive type of carbon with a higher activity and surface area was required. Sontheimer found that it was more economical to regenerate carbon on site than to transport it to a carbon-producing company.

Reactivation of granular carbon is an important factor in cost and design. The objective of regeneration is to remove the adsorbed materials from the carbon porous structure, thereby reinstituting its ability to adsorb impurities. Common methods include thermal or steam treatment, solvent extraction, acid or base treatment, and chemical oxidation (Ford, 1981). Reactivation of powdered carbon has also become commercially accepted (Hutchins, 1981).

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[5] Molasses number refers to the milligrams of molasses adsorbed during standard test and measures the volume of pores greater than 28A° in diameter. Carbons with a high percentage of this size would be suitable for adsorbing high molecular weight substances (Benefield *et al*., 1982).

Granular Activated Carbon (GAC)

Odour free water has been produced in laboratories by GAC for many years. The procedure is convenient, reliable, and capable of removing any odours remaining after other treatments (Fientje and Hager, 1964).

Advantages of GAC over other means for taste and odour removal includes:

1. its practically foolproof ability to remove taste and odour completely, or to any desired threshold value;
2. clean, simple operation requiring no adjustments to the level of raw water taste and odour changes;
3. removes all organic impurities in the water, whether or not they contribute to taste and odour; and
4. lower overall cost where rates of carbon exhaustion justify installing reactivation equipment.

Disadvantages of GAC include:

1. higher initial cost for both carbon and equipment; and
2. addition of another treatment step: GAC filtration, including, generally, a low-head transfer pumping station.

GAC beds have been used extensively in Europe, primarily to removed odours and chlorine (Woodward *et al*., 1964). In their statement regarding the use of GAC, U.S. EPA (1978a) listed over forty applications of GAC for taste and odour control in the U.S.. GAC adsorption is EPA's preferred method for removing organic contaminants because it removed many compounds, including both trihalomethane and their precursors (Mullins *et al*., 1980). Pressure type GAC filters are used extensively by the bottling industry for quality control (Rosen and Booth, 1971).

The main advantage of GAC over PAC is that GAC has a more efficient adsorption capacity. Snoeyink (1976) illustrated this by using adsorption of methylisoborneol (MIB) as an example. To lower 10 ug/L MIB to its Threshold Odour limit of 0.1 ug/L, by PAC adsorption, an equilibrium had to be reached throughout the water before the carbon settled to the bottom of the sedimentation tank. The amount of MIB adsorbed would be 0.3 mg/g. Snoeyink found a carbon dosage of 33 mg/L was required. Carbon beds, on the other hand, continued to operate until the effluent concentration was greater than

0.1 ug/L. Snoeyink found this equivalent to an adsorption capacity of 3 mg/L. This is in agreement with studies by Woodward *et al.* (1964).

The most common mode of application for GAC is as a replacement media for rapid sand filters (McGuire, 1980). Robeck (1975) reported that GAC filters are as effective as sand filters for the removal of turbidity, and the efficiency is greatly increased when the water is pre-treated with alum. Ferric salt has little effect on adsorption isotherms (Scheidtmann *et al.*, 1973).

Schulhof (1979) found taste problems, especially chlorine taste, to be the origin of GAC filtration development. The competition between ammonia and organic substances for chlorine is hard to determine. In many instances, this resulted in under estimating chlorine dosage, leading to the formation of odourous chlorinated organics and chloramines. Schulhof found that it was difficult to treat chlorine taste with PAC. GAC filters remove chlorine and decompose chloramine to regenerate ammonia, which is eliminated by nitrifying bacteria in the filters.

Yohe *et al.* (1980) found GAC is a very effective reducing agent of residual chlorine and chloramines. The reactions of free chlorine (at low and high pH) with activated carbon (C*) are (Magee, 1956):

Low pH: $HOCl + C^* \rightarrow C^*O + HCl$

High pH: $OCl^- + C^* \rightarrow C^*O + Cl$

The reactions of carbon with mono- and dichloramines (Bauer and Snoeyink, 1973) are:

$NH_2Cl + H_2O + C^* \rightarrow C^*O + NH_3 + HCl$

$2NH_2Cl + C^*O \rightarrow N_2(gas) + H_2O + 2HCl + C^*$

$2NHCl_2 + H_2O + C^* \rightarrow C^*O + N_2(gas) + 4HCl$

These redox reactions will result in a decrease in adsorption capacity of GAC for some compounds including phenols, aromatic nitro- compounds, and sodium benzene sulfonate.

Chlorination increases the surface oxides on GAC, changing the physical nature of the carbon by increasing the hydrophilicity with increased exposure, inhibiting bacterial growth, and causing a deeper initial penetration of organics at low concentration (Yohe *et al.*, 1981). The general effect of pre-chlorination on GAC was reviewed in a 1981

AWWA Committee report.

Application in Water Treatment Plants

As with ozone, GAC is often used after the conventional and less expensive methods for organics control have failed. Some of the successful application of GAC are discussed below:

France : In France, two types of GAC filters are used. The first system contained granular carbon having the same effective size as the sand it replaced, in general, 0.9 to 1.0 mm. The second system contained grains with smaller effective size, used in a two-stage role. The choice depends on the quality of treated water required. The first system is cheaper to install. Although it produced water of varying quality, general improvement can be achieved. The criterion was to produce water having an average Taste Number[4] of 2 or less. The second system produced water with constant good quality (Water Research Centre, 1977).

In the treatment of odour in the SLEE plant, the second largest water supply company in France, with sales over 850 ML in 1977, Fiessinger and Brener (1980) found that GAC had an economic advantage over powdered activated carbon (PAC) for taste removal. PAC was used during coagulation and separated in a clarifier, followed by sand filtration to give a TON of 6.9. Two-stage GAC filters, with regeneration every five years, can produce an average odour threshold of 2.5. This is equivalent to a PAC treatment of 20 mg/L.

Virginia : In 1960, the Town of Hopewell Va., installed two GAC filters and were able to remove odours which were not practical to remove by other methods at filtration rates as high as 440-490 Lpm/m² (9-10 gpm/ft²). PAC doses as high as 100 mg/L were not effective under the conditions at Hopewell (Flentje and Hager, 1964). A filtration rate as high as 30 m/h is acceptable for taste and odour elimination in some installations (Rice *et al*., 1978b).

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[4] Taste Number: The number of subsequent halvings of the concentration of a sample by tasteless water before the sample is judged to have no taste (Water Research Centre, 1977)

California : Pressure GAC filters following diatomaceous earth filters were used by the Goleta Water District in California to control sulfide odours caused by hydrogen polysulfides. The system, however, was only able to give an effluent TON of 0 to 35 when the influent TON varied from 6 to 1,000 (Lawrence, 1968; Monscvitz and Ainesworth, 1970).

Michigan : To control taste and odour at Mt. Clemens, Michigan, Hansen (1972) found that 100 to 150 mg/L PAC were required. The odour originated from septic and phenol pollution, and algae and actinomycetes products. Installation of GAC filters in 1968 had eliminated all taste and odour problems. Regeneration was required after three years of operation, representing an operating cost of US$4.75/million gal. of water treated and an equivalent dosage of 2.6 mg/L of carbon. GAC also removed pesticides, detergent and all inorganic heavy metals (Hansen, 1973).

Switzerland : The operating time of GAC for a Swiss Lake water was only six months when ozonation was not used. When the ozonation process was placed before GAC filtration, the GAC could be used for about three years. The six-fold increase in GAC operating time contributed significantly to the economy and efficiency of plant operation (Schalekamp, 1979b).

Ohio : Love *et al*. (1974) reported on the treatment of odour at Piqua, Ohio, where 51 cm of sand in an 81 cm deep rapid sand filter was replaced by GAC. After 33 months, the beds were still producing odourless water but the capacity for the carbon-chloroform extract (CCE) was exhausted after only ten weeks of operation. Previous attempt to control odours by PAC required dosages over 100 mg/L.

Massachusetts : GAC filters were installed to control taste and odour at Lawrence, Massachusetts. To avoid any problems with particulate (turbidity) breakthrough, sand was left in the bottom of the new GAC filters. A six month comparision of the turbidity in the effluent of a conventional sand filter and an all granular activated

carbon system showed that their performance was equal. Granular activated carbon has now completely replaced the sand filters (Love *et al*., 1974; Love and Symons, 1977). Similar results were also observed by Hansen (1973).

The U.S. EPA s *Interim Treatment Guide* (USEPA, 1978b) also reported on the ability of GAC to control taste and odour to give effluent TON values of less than 1 for one year, when the influent TON ranges from 6-10. Surveys by Ford (1974) in the U.K. and Symons (1976a) in the U.S. showed the shortest effective life reported for GAC to be twenty-three months. Some beds had been in service for four years and were still effective.

In the removal of specific organics, Gauntlett and Packham (1973a) reported on the strong adsorption of chlorophenols by activated carbon at the ug/L level, which is near the Threshold Odour limit for these compounds. As the number of chlorine atoms substituted on the phenol increases, the solubility of the neutral species decreases, and the adsorbability increases. The pKa of the species, however, also decreases with the increased chlorine substitution, thus lowering the pH at which the species exist in anionic form. This would enhance the adsorption, since Murin (1974) has shown that pH values lower than the pKa can result in better adsorption. Humic substances and other chlorophenol species may interfere with activated carbon adsorption. It has been reported that the bed life for chlorophenol adsorption will be greater than for MIB and much greater than for humic substances (U.S. EPA, 1978a).

GAC is also effective in the removal of industrial odour caused by compounds such as *bis*-(2-chloroethyl) ether, 2-ethyl hexanol, *bis*-(2-chloroisoproply) ether, methylbenzyl alcohol, acetophenone, isophorane, and tetralin at concentrations of 10-100 ug/L. Dostal *et al*. (1965) found that a finer carbon, 20x50 mesh, can produce an odour free water for twice as long as an 8x30 mesh carbon.

With the increasing application of GAC in water treatment plants, there is a need for a more effective monitoring system. Robeck (1975) found that odour breakthrough, probably of biological origin, occurs much later than the breakthrough of general organic compounds. The removal of odour can be sucessful for years, whereas the deterioration

of the organic removal as indicated by carbon-chloroform extract or carbon-alcohol extract will occur after a few weeks. McCreary and Snoeyink (1977) attributed this to the intermittent nature of the biological odour problem and also to the fact that compounds causing odours were generally present at low concentrations. These findings were in agreement with those of Love *et al*. in 1974.

Ford (1974) summarized the effectiveness of GAC for taste and odour control by defining three different phases:

1. a period of at least four months when even intense taste is completely removed;
2. a middle phase of about 18 months when taste removal, although partial, is still effective in preventing consumer complaints; and
3. a final period when taste removal is still taking place, but peaks of taste activity will produce breakthrough and consumer complaints.

In his paper on GAC filter design, Sontheimer (1979b) recommonded a filtration velocity of 20-30 m/h, a bed height of 2-3 m and an empty bed retention time of 6-10 minutes for taste and odour removal. Filter beds are normally placed after conventional filtration systems, and can be used without prior water treatment if the influent is relatively clear (Rosen and Booth, 1971). The use of chlorine dioxide with GAC was also found to be effective for TOC and trihalomethane precursors removal (Lykins and DeMarco, 1983). The application of ozone with GAC is discussed under the heading of BAC.

Powdered Activated Carbon (PAC)

The advantages of PAC in taste and odour control lie in the possibility of adjusting to the type and concentration of the disturbing substances, and in the lower investment cost (Sontheimer, 1979a). An AWWA Committee in 1977 found that approximately 25% of the 645 U.S. utilities surveyed used PAC for taste and odour control.

There are two types of PAC feed systems used in water treatment: a slurry tank and an elevated, dry carbon storage bin. In a slurry tank, carbon is maintained in a suspension of 0.1 Kg carbon/L (1 lb/gal) of water. In the storage bin, the dry carbon is withdrawn from the bin as needed and wetted in a wet down cone. The slurry solution is

then injected as required (Nielsen and Whipple, 1979).

In their study to control taste and odour at the Orinda Plant in California, Nielsen and Whipple (1979) found that a dry storage system was easier to control and construct than a slurry tank. 10-20 mg/L PAC was required to treat water with Threshold Odour Numbers ranging from 4 to 8.

Generally, carbon should be applied first; after a suitable contact period, the oxidant can be added. Reversing this sequence can lead to an increased odour problem (Hyndshaw, 1972). A contact time of 10 to 15 minutes or more was recommended by Hyndshaw (1962). He also pointed out that the addition of softening chemicals will raise the pH of the water, making it more difficult for carbon to adsorb odorous organic compounds. In general, more carbon is required when chlorine is applied before carbon addition. Sigworth (1961a) suggested the addition rate of PAC to the filter influent should not exceed 6 mg/L except for short periods and only if the sand filters are in excellent condition. In a later report (Sigworth, 1961b) he suggested larger doses of carbon should be added at the mixing basin, allowing the carbon particles to settle out with the floc to stabilize the sludge in the settling basin.

Application of PAC at points prior to filtration, or if no filters are used, prior to coagulation, was also recommended by Sigworth (1956). If the odour develops suddenly, Sigworth recommeded addition to the top of the filter or to the filter influent. This method was also effective for the removal of low concentration odour or odour which appear at infrequent intervals. The maximum dosage recommended for filter application was 6 mg/L.

Sigworth (1956) pointed out that activated carbon was most effective at pH values below 9.0. Odourous compounds may form salts at higher pH, making them more resistant to adsorption. For this reason, carbon should never be mixed with alkaline material such as lime or soda ash.

PAC has been in use in Suresnes-pont-Valerien, France, for the control of taste since 1959. Seven other plants also used PAC for the removal of tastes and organics with dosages up to 40 mg/L (Schulhof, 1979). PAC was very effective in eliminating tastes from treated water containing low concentrations of organic substances and ammonia, and was especially adapted to meeting organic matter concentration peaks of short

duration without large capital costs. Schulhof also found that the carbon should be introduced last, as far as possible from the flocculating agent, chlorine and chlorine dioxide. Adding the carbon at two different locations improved the economy of treatment. However, the increased organic and ammonia loading in the raw water over the long term, and the constant increase of chlorine can create taste problems that PAC cannot eliminate.

Carns and Stinson (1978) found PAC to be ineffective in reducing trihalomethane. They reported, however, that PAC will not pass through filters even without sedimentation. They theorized that PAC served as nuclei for flocculation and, therefore, did not pass through the filters. On the other hand, rapid floc growth on PAC particles may shield carbon from dissolved organics in raw water, limiting its effectiveness in the reduction of trihalomethanes and TOC.

As would be expected, the amount of carbon that must be added is dependent on the odour-causing compounds. In his study, Hyndshaw (1972) found that 40 mg/L PAC was required to reduce 6 mg/L of 2,4 D from a TON of 50 to 3. The presence of 5 mg/L of DDT which gave a TON of 70 required only 4 mg/L to give the same effluent TON. These pesticide concentration are, of course, far above those that would be anticipated in potable water treatment. In lab scale studies of PAC, Duke *et al*. (1980) found that the amount of PAC required to remove 50% of the trihalomethanes was 45 mg/L, a concentration that is not economically feasible.

Hoehn *et al*. (1977) found the most effective dose of PAC to be 50 mg/L, regardless of the point of application. A more recent study by Anderson *et al*.(1981) found that by using a PAC formulated for THM precursor reduction, a dosage of 21.6 mg/L PAC could give 56% THM reduction. Laboratory tests used to determine the optimal dosages of activated carbon required for producing palatable water were presented by Rosen and Booth (1971). A survey of 54 surface supply water treatment plants found that PAC was used at dosages varying from 0.25 to 60 mg/L with a median of 5 mg/L (AWWA, 1976).

Flentje and Hager (1964) found that a comparision of GAC and PAC doses needed for taste and odour removal treatment was difficult to make because carbon filters, at least during a considerable portion of a run, completely remove taste and odour, whereas

PAC was generally used to produce a threshold value acceptable to the customers. PAC is cheaper than GAC and extensive plant construction costs are not required (McCreary and Snoeyink, 1977). However, after installation, GAC avoids the requirment of constant testing and adjusting of carbon feeds, and the problems with PAC penetration of filters (Hansen, 1972). Excessive filtration rates, alum colour floc or polymers may decrease the effectiveness of GAC and favour the use of carbon slurry (AWWA, 1976).

Other advantages of GAC over PAC listed by Schuliger (1978) included:

- problems with disposal of PAC and filter cake;
- greater labour requirements for the PAC system;
- higher product losses per weight of carbon used; and
- inefficient use of the carbon.

Based on these findings, it would appear that PAC is more desirable only if the carbon is needed on an infrequent basis throughout the year.

Degremont (1979) found that if only 15-20 g/m^3 of PAC were required, its use in a clarifier was more economical than that of a GAC bed. If PAC had to be used in large doses from time to time, or if it did not eliminate all taste, combining a small dose in a clarifier with final ozonation was usually effective. The cost of producing three grams of ozone is about the same as the cost of ten grams of PAC (Degremont, 1979). In Europe, GAC is used if large doses of PAC (>20 mg/L) are required (Water Research Centre, 1977).

Biological Activated Carbon (BAC)

Biological activated carbon is a term to denote a train of unit processes including pre-treatment by ozonation, followed by a GAC column which shows significant aerobic bacterial activity (Rice *et al.*, 1977). Filtration through an inert medium (sand or anthracite) and aeration before the GAC column may also be included (Miller *et al.*, 1980; Rice and Browning, 1981). Although biological activity can occur in GAC or sand filters without pre-ozonation, it is maximized when ozone is used (Miller *et al.*, 1980). The process promotes the growth of aerobic bacteria on both the inert media and GAC filters. These aerobic bacteria simultaneously reduce the levels of dissolved organic carbon (DOC) and

ammonia (by conversion to nitrate). The functions of ozonation are (Miller *et al.*, 1980; Rice and Browning, 1981):

1. to partially oxidize the dissolved organic materials, promoting further oxidation by the aerobic bacteria;
2. to prevent excessive growth of algae and phytoplankton in the filter media;
3. to lower the molecular weight of the non-carbon adsorbable organic materials; and
4. to raise the level of dissolved oxygen.

Miller and Rice (1978b) reported on a study by Gomella and Versanne (1977) showing that BAC was being used in Europe under relatively low organic loadings and resulting in a low organic residuals and the extension of carbon bed life up to three years without regeneration. In some situations, BAC can remove up to 86% of ammonia and 100% of the phenols.

The mechanism of BAC was explained by Guirguis *et al.* (1976c and 1980). They found that ozonation of clarified primary effluent prior to carbon treatment eliminate anaerobic conditions in the carbon columns and increased the adsorptive capacity of the carbon. Ozone oxidation, in combination with exposure to an aerobic environment, promoted biological regeneration of the carbon in the carbon bed. Guirguis *et al.* (1980) speculated that ozonation oxidized molecules which were adsorbable but resistant to biological oxidation to smaller and less complex substances which were then biodegraded.

These studies and the development of BAC were reviewed by Argo *et al.* (1980) and the AWWA Committee (1981).

There are now 23 plants in Europe with full scale BAC operation. The process is also being developed at the Cleveland, Ohio, Westerly Sewage Treatment Plant (Rice and Browning, 1981).

Adsorption vs Biodegradation

Sontheimer and Maier (1972) reported that odour removal by BAC was a combination of adsorption and biological activity. If biodegradable compounds are present in the water, some may be removed by microbial activity in the GAC beds, even if the compounds are not adsorbable. Such removal should decrease the extent of bacterial growth in the distribution system and odour problems associated with such growth. This is

of importance as many organic compounds that are resistant to carbon adsorption are biodegradable (Chow and David, 1977). Humic acid is a prime example of a substance that is not readily adsorbed by activated carbon (Kuhn *et al*., 1975; Youssefi and Faust, 1980), but can be converted to more readily biodegradable organic materials through BAC (Guirguis *et al*., 1976a and 1976c). Chloroform falls into a group of organics that is not easily oxidized and not readily converted to biodegradable materials (Miller *et al*., 1980).

The basic theory of adsorption and biodegradation by BAC is brought to doubt by some recent researches on ozonation. Benedek (1977) and the National Academy of Science (1980) found that ozone may decrease the adsorbability of some organics. Legube *et al*. (1981a) and Brunet *et al*. (1982) found that ozonation of aromatic compounds would lead to an increase in polarity and a decrease in the adsorption capacity of activated carbon. Improvement in GAC filtration, however, was attained through increased bacterial activities. Bourbigot and Dore (1982) found that the positive effect on the increased biodegradability of the organic matter in activated carbon largely offset the negative effect on adsorption caused by the increased polarity due to ozonation. The first effect is lasting while the effect on adsorption quickly fades.

The Removal of Specific Organic Compounds

The National Academy of Science (1980), Sontheimer *et al*. (1978) and Pierce (1978) reported that pre-chlorination may result in the formation of chlorinated organics that are more resistant to biodegradation on the activated carbon surface. Pierce also found that as a group, the chlorinated phenols have been identified as the halogenated organic groups possesing the strongest organoleptic properties.

Hrubec (1978) reported that ozonation after coagulation and filtration reduced the Taste Number from 12 to 4.5. Subsequent carbon filtration gave an effluent reading of 2. Similar results were obtained by Kuhn *et al*. (1975), who showed a reduction in dissolved organic content from 61 to 45 ug/L due to ozonation and to 27 ug/L if a BAC system was used.

One U.S. EPA report (1978b) also implied that precursors to trihalomethane formation were altered by ozonation in such a manner that their removal by activated carbon was made more effective. Mattson and Mark (1971) found that oxidation in a water

medium increased activated carbon hydrophilic properties. Rice (1980) found ozonation rendered humic and fulvic acid more biodegradable, meaning that biological treatment after ozonation would result in a greater removal of dissolved organic material. Cini *et al*. (1980) concluded that ozone, as a primary oxidizing and disinfecting agent, was preferred to other oxidants when used in conjunction with activated carbon. Using COD as basis of treatment effectiveness, Chedal (1976) studied various treatment methods in the removal of micropollutants. He found that ozonation and activated carbon gave 50 to 70% and 45 to 65% COD reductions, respectively. Ozone and activated carbon in combination gave 80 to 100% pollutant elimination. A slow sand filter might have to be increased 50-100 times in volume to acheive the same level of COD removal (Rice *et al*., 1978b).

Miller *et al*. (1978) reported the following criteria using DOC (equivalent to TOC) as a parameter for BAC operation :

1. water with DOC > 2 mg/L is not suitable for distribution;
2. water with DOC < 0.2 mg/L can be ozonated terminally without any real problem of after-growth;
3. application of 1 mg/L ozone per mg/L DOC results in 75% conversion of DOC to biodegradable materials;
4. application of 2 mg/L ozone per mg/L DOC results in 90% conversion of DOC to biodegradable materials; and
5. ozonated water applied to a normal GAC filter will result in 30% DOC removal across the carbon unit process, corresponding to between 100-200 g DOC removed per cubic meter of GAC (BAC) per day.

The use of BAC may be more cost effective than GAC filters alone (Clark and Dorsey, 1980).

BAC has been seen as a replacement for activated carbon columns which in many instances, have been reported to be the source of sulfidic odours in water and wastewater treatment (Guirguis *et al*., 1976b; Directo *et al*., 1977; Monscvitz and Ainesworth, 1970). The odour originates from anaerobic activities on carbonaceous matters.

Application in Water Treatment Plants

The BAC system is used at Mulheim-en-der-Ruhr in Germany, to eliminate breakpoint chlorination in the treatment of polluted surface water, and to avoid production of organochloro compounds. Sontheimer *et al.* (1978) reported that a system consisting of flocculation, sedimentation, ozonation, filtration and activated carbon treatment, could significantly reduce dissolved organic carbon and UV absorbance value.

Fiessinger and Brener (1980) examined the effectiveness of BAC at Morsang- Sur-Seine Water Treatment Plant in France. In this study, four treatment lines were established:

1. raw water- breakpoint chlorination- sedimentation with PAC- sand filtration- ozonation;
2. raw water- breakpoint chlorination- sedimentation- sand filtration- ozonation- GAC filtration;
3. raw water- breakpoint chlorination- sedimentation- sand filtration- GAC filtration- ozonation; and
4. raw water- sedimentation- sand filtration- ozonation- GAC filtration.

The raw water exhibited a TON of 12. After treatment, Line 1 gave a TON of 2, while Lines 2 and 4 gave zero TON. Line 3 gave zero TON after GAC but the level increased to 1.5 after ozonation. Line 4, without chlorination, also gave the lowest trihalomethane residual. The lines were evaluated after 35 months of operation, and found that the GAC contactor receiving ozonated water gave better results than the one receiving unozonated water. The increase in organic compound removal with ozonation prior to adsorption was in contrast to the negative effect of oxidants on carbon adsorption as demonstrated by McGuire *et al.* in 1978. Fiessinger and Brener concluded that results comparable to Line 4 might be obtained with PAC at a higher dosage but greater operational cost. In a separate report on the same study, Richard and Brener (1980) found that Line 2 reduced the Taste Threshold from 12 to zero. Lines 1, 3 and 4 had remaining Taste Thresholds of 1 to 2. However, Line 1, with 10 g/m^3 PAC, gave 71% trihalomethane potential reduction compared to 70% with Lines 2 and 3.

Miller and Rice (1978b) summarized their survey of water treatment plants in Europe and found ozone or BAC to be the best technique(s) available for reduction of organic concentrations in drinking water. They recommended a process train consisting of

screening- flocculation- sedimentation- rapid sand filtration- ozonation- granular activated carbon- chlorine or chlorine dioxide to give safe drinking water form polluted source.

The advantages of BAC have been studied by many workers and can be summarized as follows (Rice, 1978; Rice *et al.*, 1978a; Rice *et al.*, 1978b; Miller *et al.*, 1980):

1. more effective removal of dissolved organics from solution (up to 200% greater);
2. increased capacity of the carbon to remove organics (by a factor of about 10);
3. increased operating life of the activated carbon columns before reactivation, especially if the GAC can be kept free of halogenated organics (partial biological regeneration);
4. biological conversion of ammonia (nitrification);
5. use of less ozone for removing a given amount of organics than with ozonation alone (BAC is more cost-effective over ozonation in removing dissolved organic); and
6. abilities to treat filtrates from BAC columns in drinking water plants with only a small quantities (0.1 to 0.5 mg/L) of chlorine or chlorine dioxide to produce a water of acceptable bacterial quality and provide a residual disinfectant to the distribution system.

It is of interest to note that recent research has brought on many questions regarding the validity of the BAC concept in water treament (Benedek *et al.*, 1983).

Toxicity

In their presentation to the U.S. EPA regarding the use of GAC for removing trihalomethane, Pendygraft *et al.* (1979a) pointed out many unknown and toxicity factors regarding the use of activated carbon. These include:

1. the finding of eighteen suspected carcinogenic inorganic elements such as lead, mercury and cadmiun in a composite sample of GAC;
2. the presence of ten distinct polycyclic aromatic hydrocarbons (PAH) in twenty-two different powered and granular activated carbons tested (Borneff, 1980);
3. the formation of PAH and other toxic materials through consecutive carbon regeneration;

4. the leaching of heavy metals from GAC.
5. the formation of chlorinated compounds after exposing GAC to >100 mg/L chlorine.
6. the formation of harmful substances through localization and catalytic action of GAC (Cookson, 1978), and
7. microbial growth.

Lange and Kawczynski (1978) reported on the increase in trihalomethane concentration at higher carbon doses (40 to 50 mg/L). Recently, Chen *et al.* (1982) reported on the formation of halogenated compounds when chlorine dioxide is used in conjunction with activated carbon.

Suffet (1980) also raised many questions regarding the use of GAC. He pointed to the necessity to identify compounds that are retained on, or released from GAC, and organic compounds that may be formed from natural precursors by microbial activity on the GAC filters. Although no pathogenic microorganisms have been isolated, both gram-negative rods (Brewer and Carmichael, 1979) and gram-positive rods, cocci and mold (Fiore and Babineau, 1977) had been found on GAC.

A 1977 U.S. EPA (1977a) report provided data to deny the presence of gram-negative bacterial endotoxins, leaching of metals and inorganic elements from GAC beds. Suffet (1980) found endotoxins that were produced were at such low concentrations that they possed no health risk. Leaching will occur when the carbon is boiled with acid. Bacterial sloughing from carbon filters was negligible based on a study by Donlan and Yohe (1983). Borneff (1980) also showed that PAH desorption did not occur in GAC filters.

Many toxic compounds, such as beryllium, barium and selenium have low or unknown adsorption potential (Sigworth and Smith, 1972). PAC also should not be allowed to mix with chlorine bearing compounds in the dry state as the subsequent chemical reactions can be sufficiently violent to cause an explosion (Sigworth, 1956).

In his report, Cookson (1980) found that catalytic reactions on the surface of activated carbon were most likely to involve localized defects caused by impurities in the carbon structure or through adsorption of metals, oxides and other substances. Oxidation, reduction and polymerization reactions can produce new organic and inorganic

compounds. These compounds may be released into the water and behave as typical solutes in their adsorption equilibria and competition for carbon sites. Cookson concluded that although there were insufficient studies regarding activated carbon catalyzed reactions, no harmful chemicals are known to have resulted from activated carbon application to water treatment.

Occupational Health

Strudgeon *et al*. (1980) pointed out many operational problems of using activated carbon. These include:

1. dust contamination: airborne dust which can be a potential contaminant to personnel by contact with skin, eyes and respiratory systems;
2. dust explosions;
3. hazardous environments: production of hydrogen sulphide and methane from anaerobic bacterial growth and adsorption of atmospheric oxygen by wet carbon (two deaths and several injuries have been reported when individuals entered carbon contacters without adequate protection); and
4. equipment failures: concrete and fiberglass are resistant to activated carbon, but even the reinforcing steel in concrete is subject to attack by galvanic corrosion.

At the Orinda plant in California, special systems for carbon handling, dust collection and sprinklers were required to minimize handling, dust pollution and fire hazard. Since PAC can be corrosive in the presence of moisture, all motors and electrical wiring had to be checked against the danger of explosion (Nielson and Whipple, 1979).

Freshly activated carbon will, within a matter of minutes or hours, adsorb significant quantities of oxygen. This will be accompanied by a modest rise in temperature. Activated carbon will react with oxygen to give carbon monoxide and carbon dioxide. The rate of reaction is governed by the temperature. If the heat generated is not dissipated, the rise in temperature will increase the reaction rate and can lead to auto-ignition (Akell, 1981).

Safety in handling, transportation and design of activated carbon systems was discussed by Strudgeon *et al*. (1980) and Akell (1981).

Conclusion

PAC is usually the first method to use for taste and odour control. It is relatively inexpensive, easy to handle and safe. Although PAC can give satisfactory results, other methods should be considered if the PAC dosage exceeds 20 ppm.

BAC can be considered as the best available method for organics, taste and odour removal. Until new research can dispute the present findings, it can be stated that the ozonation of GAC can enhance organic removal as well as prolong carbon bed life. Dispite the high cost of a BAC system, it must be given consideration if required by the deteriorating raw water quality.

IV. PILOT PLANT DESIGN

In order to achieve the objectives of this study, the pilot plant was designed to allow for comparison studies on the two oxidants, granular activated carbon after different type of oxidation reactions, and granular activated carbon adsorption with or without preoxidation. The systems were operated in batch mode because of manpower limitations.

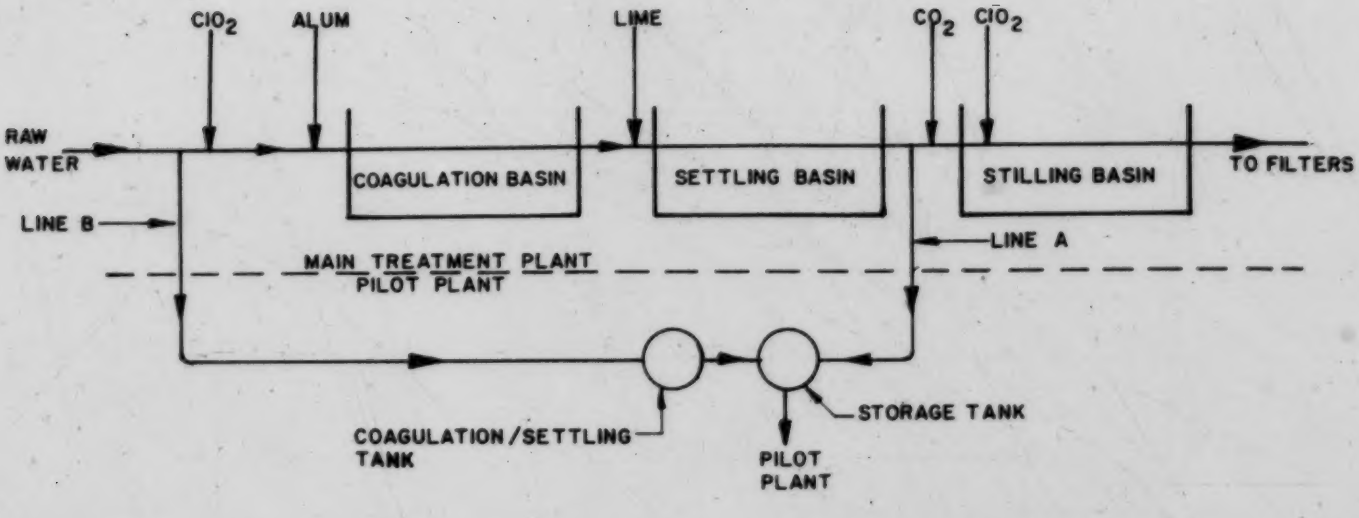
The pilot plant was located in the north east part of the Rossdale Water Treatment Plant next to the chlorine dioxide operations room. Water for testing was obtained from the recarbonation chamber of Plant no. 1 of the main Treatment Plant, or from a raw water line (Diagram 1). With the two inlets system, the pilot plant had the capacity for conducting two stage oxidant addition tests or pre-oxidation studies of raw water by ozone or chlorine dioxide.

The treatment plant water intake line (Line A) was designed to take in water after partial treatment by the main plant. Water, which had undergone coagulation and settling, was pumped from the recarbonation chamber, just prior to the addition of chlorine dioxide. This line allows the direct comparison of the results between the oxidation processes in the main plant and the pilot plant.

During spring runoff, the raw water line (Line B) became necessary when the main plant began the addition of chlorine dioxide into the raw water prior to alum addition. With the presence of about 0.2 to 0.6 ppm chlorine dioxide in the water, further treatment by chlorine dioxide or ozone would not give meaningful results. Raw water was therefore diverted into the pilot plant from a point prior to chlorine dioxide treatment. The water underwent a batch coagulation process in the pilot plant and was then transferred into the storage tank. A surrogate chemical, if used, was added to the water in the storage tank.

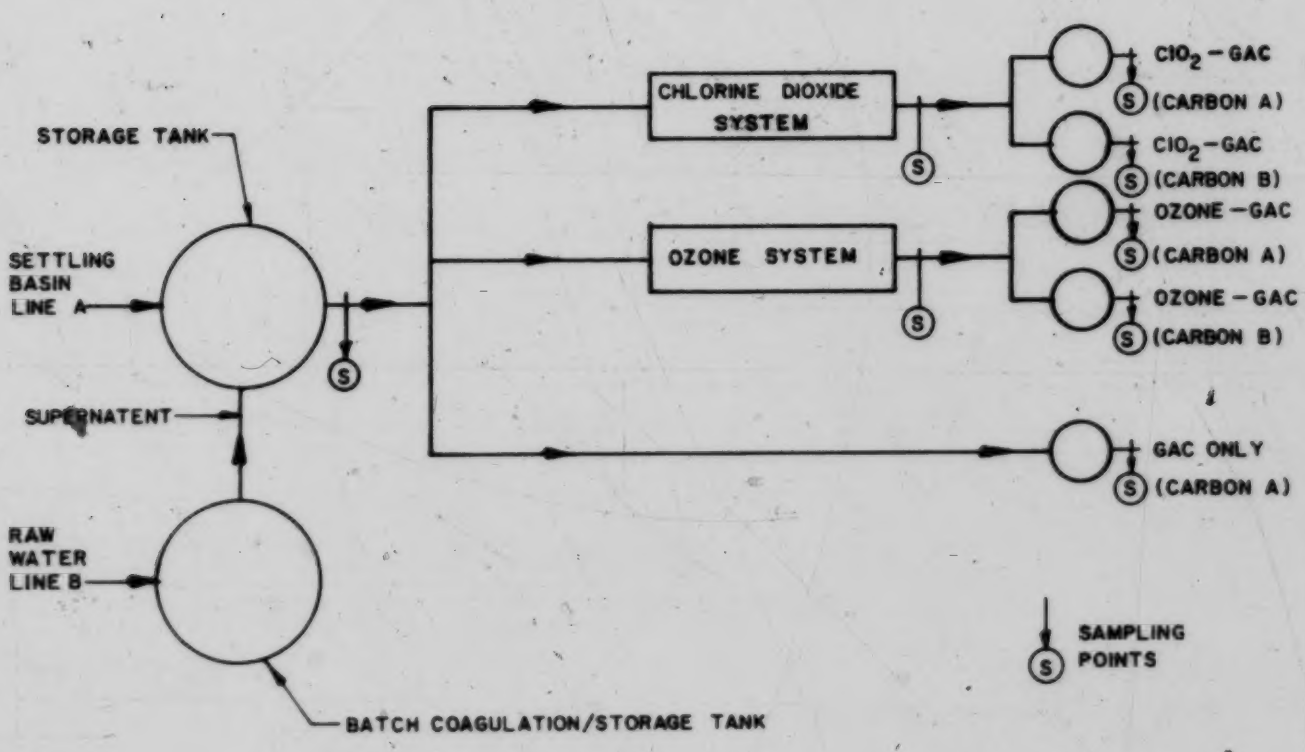
From the storage tank, water was diverted into three parallel streams of the pilot plant: chlorine dioxide, ozone and granular activated carbon systems (Diagram 2). After oxidation by chlorine dioxide or ozone, the effluent was pumped to its respective granular activated carbon columns. Sampling points were established in the storage tank, after oxidation and after activated carbon treatment. All the tanks were cleaned with service water daily. Control studies showed that the cleaning method was adequate in eliminating any chemical residual from the previous day. The pilot plant used the 12mm teflon tubing.

Leroy-Somer Moteur Asynchrone Rotor diaphram pumps and PVC true union ball valves for flow transport.



WATER INTAKE SYSTEM FOR PILOT PLANT

DIAGRAM - 1



SCHEMATIC PILOT PLANT FLOW DIAGRAM

DIAGRAM - 2

V. SYSTEM COMPONENT OPERATION

A. Coagulation System

The main objective of the batch coagulation system was to provide a partially treated water supply as a testing medium for the evaluation of the oxidants and activated carbon treatments. Studies on the effectiveness of the removal of the surrogate chemicals by the coagulation process were also conducted.

A 2.5m diameter and 1.5m high tank was used for batch coagulation studies. Raw water was flash-mixed with alum and then slowly stirred to allow the flocs to achieve a suitable size for settling. The alum dosage was determined by daily plant jar testing. Factorial design experiments were conducted to determine the optimal conditions for the coagulation-flocculation process.

The experiments were set up to determine optima for

1. rapid mix time;
2. rapid mix speed;
3. Flocculation time;
4. Flocculation speed; and
5. Settling time

Parameters such as turbidity, suspended solids and pH were monitored. From the information gathered, it was possible to produce a treated water with suspended solids and turbidity removal equivalent to, or slightly better than that of the main plant's. pH readings were also the same for both processes after alum addition. However, the pilot plant treatment was not as effective when the raw water turbidity was less than 10 NTU.

The procedures established from the factorial experiments were as follows:

To begin operation, the coagulation/settling tank was filled from Line B with 2000 litres of raw water. The variable speed mixer was then set at a rapid mix speed of 700 rpm. At that speed, the 250 mm flat blade marine propeller provided rapid surface movement with slight eddies. Alum was added at the point where the mixer shaft broke the water surface. After 135 seconds of mixing, the mixer speed was slowed down to a 180 rpm for 27 minutes. After

settling for 45 minutes. 1700 litres of the supernatant was then transferred to the storage tank by a centrifugal pump with an inlet held 75 mm below the water surface by a flotation device.

B. Chlorine Dioxide System

Chlorine dioxide is being generated at the Rossdale Water Treatment Plant by the use of generators supplied by the Rio Linda Chemical Company in California. The system uses 25% liquid sodium chlorite and gaseous chlorine to produce chlorine dioxide (Aieta and Roberts, 1981).

For this study, the main plant chlorine dioxide concentration was determined and a portion of the chlorine dioxide was then diverted into a 150 litre container in the pilot plant. The chlorine dioxide was then diluted with service water to give the desired concentration.

$$\text{Dosage of } ClO_2 \text{ applied in pilot plant (mg/L)} = \frac{\text{conc. of diluted } ClO_2 \text{ Solution (mg/L)} \times ClO_2 \text{ pumping rate (L/min)}}{\text{Water flow rate (L/min)}}$$

The chlorine dioxide pumping rate varied from 0.2 to 0.5 L/min, depending on the required dosage. Adjusting the pumping rate could compensate for the decrease in chlorine dioxide concentration with time.

Chlorine dioxide was added and mixed with the incoming water before entering the contact tank (Diagram 3). The plexi-glass tank acted as a contact tank as well as a retention chamber. A water flow rate of 4.2 L/min resulted in a contact time of 60 minutes. Effluent was pumped at a rate of 1 L/min into the activated carbon columns. Excess water was diverted into an overflow drain (Diagram 3).

The chlorine dioxide concentration was determined by the use of a Pye Unicam SP8-500 UV/VIS Spectrophotometer set at 360 nm. The chlorine dioxide residual was determined by titrating 200 mLs of the effluent with 0.00564 N phenylarsine oxide at pH 7, in the presence of KI, using a Wallace-Tiernan amperometric titrator (APHA, AWWA and WPCF, 1980).

C. Ozone System

Ozone was generated from a Union Carbide ozone generator (Model SG-4060). Low dew point (-40°C) oxygen was converted to ozone by the application of 120 watts to the dielectric and metal electrodes.

The flow of ozone into the pilot plant was controlled by adjusting the gas flow out of the sampling valve of the generation unit. Ozone entered a stainless-steel contact chamber and was mixed with the influent by a six-paddle type mixer. The unit (Diagram 4) was designed and used in a previous University of Alberta project (Caverson, 1983). Ozonated water then entered a fiberglass retention tank where the retention time was governed by the water flow rate. The combined volume of the two tanks was 240 litres. The ozone system was connected to the activated carbon system in series. Water entered the activated carbon columns at a flow rate of 1 L/min and excess water flowed into the drainage system. Excess ozone or off gas flowed into either the main plant's clarifier for dispersion or entered a sodium thiosulphate scrubber system in the pilot plant.

The ozone gas, off gas, and residual concentration was determined by reacting with 0.1 N potassium iodide solution, and subsequent titration with phenylarsine oxide using amperometric titration method at pH 4 (APHA, AWWA and WPCF, 1980). Water flow was monitored by calibrated rotometers.

$$\text{Dosage of Ozone applied in pilot plant (mg/L)} = \frac{\text{titration volume(mL)} \times \text{conversion factor(4060.8)}}{\text{volume of sample (mL)} \times \text{water flow rate (L/min)} \times \text{time of reaction (seconds)}}$$

D. Granular Activated Carbon System

The granular activated carbon (GAC) system consisted of five plexi-glass cylinders 2.2 m (7') height and 100 mm (4") inside diameter. An average carbon bed depth of 1.5 m (5') was used to allow for bed expansion during backwashing (U.S. EPA, 1973) (Diagram 5). Water entered the columns in an upflow mode at a rate of 1 L/min. Five sampling ports consisting of 3.2 mm (1/8") diameter stainless steel pipes were located at 200 mm (8") increments from the bottom. Two types of carbon, Pacific Carbon (Pacarb 800) and Calgon, were used. 12 x 40 mesh carbon was used for the upflow bed because a lower

upflow velocity is required for bed expansion than with larger carbon. All the columns were connected to a backwash system which allowed for the backwashing of any one or all of the columns. In-line rotometers monitored the flow into all columns. Specification of the columns are given in Table 2.

Table 2. Specification of GAC Columns

Columns

Diameter : 101.0 mm (4 in) i-d

Depth : 2.2 m. (7 ft)

Surface Area : 810.7 cm^2 (0.087 ft^2)

Volume : 0.015 m^3 (0.52 ft^3)

Carbon

Type : 12 x 40 mesh

Depth : 1.5 m (5 ft)

Volume : 0.012 m^3 (0.44 ft^3)

Hydraulic Parameters

Surface Loading : 122.3 Lpm / m^2 (2.5 Imp. gpm / ft^2)

Flow Rate : 1.0 L / min (0.218 Imp gpm)

Filtration Rate : 7.4 m / h (24.28 ft / h)

Volumetric Loading : 79 Lpm / m_3 (0.495 gpm / ft^3)

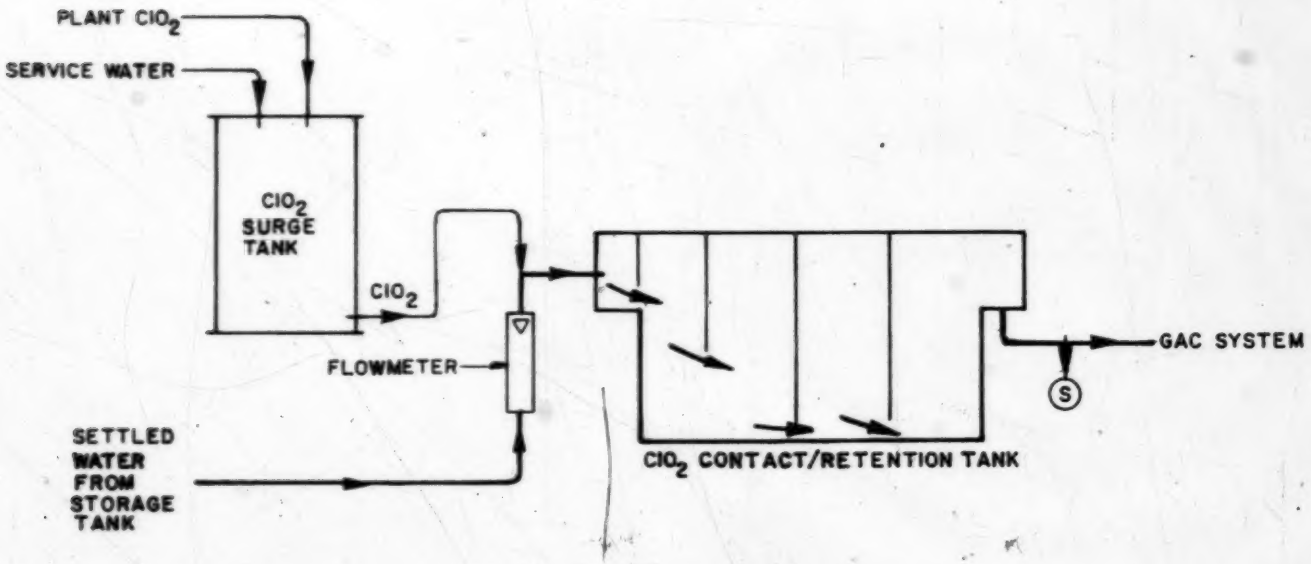
EBCT : Filter Bed Depth (m) / Filtration Velocity (m / h) = 12.3 min

Bed Expansion : @ 122.3 Lpm / m^2 (2.5 Imp. gpm / ft^2) @22°C = 2%

Backwash

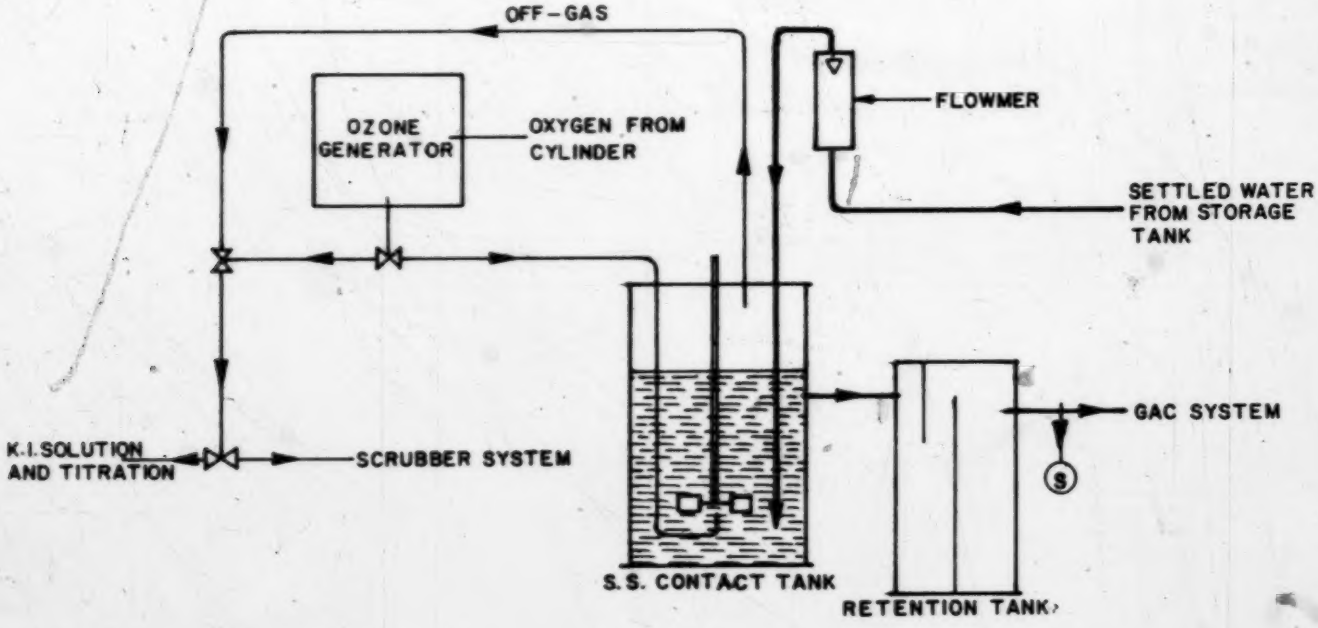
Expansion : @ 489.3 Lpm / m^2 (10 gpm / ft^2) @ 22°C = 30% (0.46 m or 1.5 ft headspace) with approx 14.5 cm (1.74") water / ft of bed depth headloss

Water Storage : @ 3.96 L / min (0.87 gpm) for 20 min requires 80 L (1.22 m x 0.3 m tank for 0.09 m^3 volume)



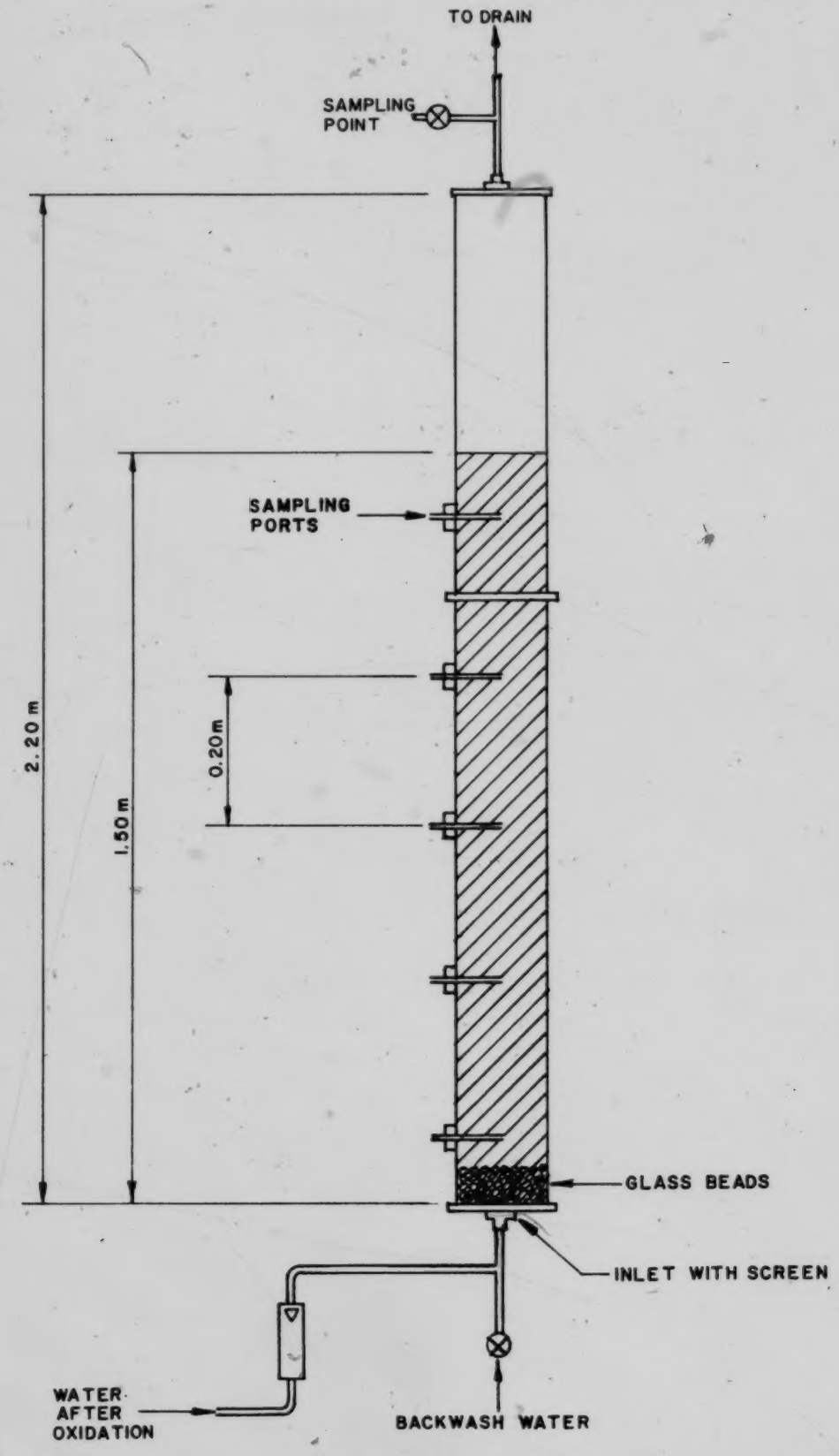
CHLORINE DIOXIDE SYSTEM

DIAGRAM – 3



OZONE SYSTEM

DIAGRAM – 4



GRANULAR ACTIVATED CARBON SYSTEM

DIAGRAM – 5

VI. TESTING PARAMETERS AND ANALYSIS

Many physical and chemical parameters were monitored at different stages in the pilot plant. Samples were obtained after oxidation and activated carbon treatment to give an indication of the effectiveness of various unit processes.

Physical parameters studied included temperature, colour, turbidity, and suspended solids. Chemical properties monitored were pH, TOC, and volatile organic compounds using gas chromatography.

Colour, TOC and GC analyses were carried out by the laboratory staff at the Rossdale Water Treatment Plant. Other analyses were conducted by the pilot plant operator. The procedures for all the testing methods used are outlined in *Standard Methods* (APHA, AWWA and WPCF 1980). The equipment used are listed in Table 3.

Table 3. Parameter and Equipment Used in Pilot Study

Parameter	Equipment	Specification or Method
Turbidity (NTU)	2100A Hach Turbidimeter	
Suspended Solids (mg / L)	Drying oven	125°C
Colour (TCU)	Spectrophotometer	450 nm
pH	Fisher accumet model 425 Digital pH / ion meter	
TOC (mg / L)	Photochem Sybron Barnstead Automatic TOC Analyzer	
Volatile Organics (ug / L)	Hewlett Packard 5830A Gas Chromatograph	purge and trap
Temperature	thermometer	

VII. SURROGATE CHEMICAL

Although the pilot plant was designed to test the runoff water, low runoff during the testing period had limited useful data available. In order to gather more information on the reactions of the taste-andodour-causing chemicals, and to provide a realistic, yet controlled experiment, surrogate compounds were used.

A GC-MS analysis of the raw and treated water was carried out in the spring of 1982. A total of 250 compounds were found in the water. However, the concentration of these chemicals were present in such low levels (3 to 175 ppb), and close to the detection limits, that only half (102) of which were named. Only five priority pollutants as classified by U.S. EPA were detected (Walker, 1983).

The major classes of chemicals identified are listed in Table 4. Based on the study, the monitoring of the following compounds in both raw and treated water was recommended:

ethylbenzene
1,2-dimethylbenzene
1,4-dimethybenzene
2-(2-ethoxyethoxy)-ethanol
nonanol
tridecane
tetradecane
2-chloro-4-(1,1-dimethylpropl)-phenol
pentadecane
hexadecane
heptedecane
octadecane
nonadecane
eicosane

Ethylbenzene was chosen as the first surrogate chemical because it is a known organoleptic and toxic compound. Ethylbenzene was also readily available for testing. It can be analyzed by GC, using the facilities available to the pilot study, within a resonable time and a high degree of accurracy.

Ethylbenzene (ethylbenzol, phenylethane) is a colourless, flammable liquid with a pungent odour. It has many industrial uses, including the manufacturing of cellulose acetate, styrene and synthetic rubber. It is also used as a solvent or diluent, and as an anti-knock agent in automotive and aviation gasoline.

Ethylbenzene may enter humans through ingestion, inhalation, or percutaneous routes. The mode of action includes irritation, depression of the central nervous system

causing pulmonary edema, as well as hepatitis. The TLV is set at 100 ppm (435 mg/m^3) (Plunkett, 1976; Sitting, 1979) while the organoleptic limit is set at 0.1 mg/L (Verschueren, 1977). A TON of 0.1 to 0.4 mg/L was reported by Verschueren (1977). Concentration of 0.25 mg/L can cause the tainting of the flesh of fishes and other aquatic organisms (Verschueren, 1977).

Levels	HC	Aromatic	-OH	Paraffin	Alicyclic	Phenolic	Others
1	9	9	2	15	3	3	8
2			3	5		1	1
3		2	11	16	5	1	7
4							
5							2

Table 4. Identification and Frequency of Families of Chemicals in the Water

Levels: Levels of confidence of identificaiton
1 - very confident, clean spectra, excellent match with library spectra
2 - some small spectra differences with library match. A good comparison. Reference standard needed for positive identification.
3 - possible compound or very similar to. Spectrum is definetely contaminated. Reference standard needed for positive identification.
4- evidence of possible structure and molecular weight. Compound not identified.
5 - unable to identify

HC: hydrocarbon, chlorinated and polynuclei
Aromatic: aromatic and chlorinated aromatic
-OH: alcohol
Phenolic: chlorinated and biphenyl
Others: ketone, diketone, ester, aldehyde, glycol, alkene, dione, diene, diyne, octyne formamdie, amine.

VIII. RESULTS AND DISCUSSION

A. Coagulation Optimization

The objective of this testing, as outlined in Chapter V, was to determine the coagulation parameters that would produce an effluent quality comparable to the main plant's. A factorial design approach was used. The initial variables and settings chosen for the factorial study are listed in Table 5. The major constrain needed in choosing the variables was to limit the total coagulation / flocculation time to less than two hours. This was necessary in order to allow sufficient time for daily testing. A setting time of 30 minutes was used for all the tests.

Table 5. First Coagulation Factorial Experiment

	Level	
Variable	- 1	+ 1
Rapid Mix Speed, rpm	900	1,200
Rapid Mix Time, min	0.5	1.0
Flocculation Speed, rpm	300	600
Flocculation Time, min	10.0	20.0

The results were unsatisfactory with no significant turbidity and suspended solid reduction. As a result, the levels for the rapid mix and flocculation speed were changed to 400-600 rpm and 100-200 rpm, respectively. The mixing time remained the same. The 125 mm impeller blade in the coagulation-flocculation tank was also replaced by a 250 mm blade to obtain better mixing throughout the tank.

The results of the second experiment showed only approximately 50% turbidity and suspended solid reductions as compared to the greater than 90% reduction obtained by the main plant's system.

Analysis of the data revealed that :

1. Flocculation time had the largest effect; the results suggested an increase in the flocculation time;
2. Rapid-mix speed had the second largest effect; results suggested an increase in the speed;

3. Flocculation speed had only a slight effect, and
4. Rapid-mix time had no effect on the turbidity and suspended solids removal. This might also indicate that the variable settings used were not within the effective range.

Based on the above findings, a third experiment was set up along the Path of Steepest Ascent. The conditions chosen and results are shown in Table 6, for a settling time of 30 minutes. It is evident that better results were obtained as the experiment proceeded along the path.

Table 6. Result of Path of Steepest Ascent Study

Trial no	RM speed rpm	RM time min.	Flocc. Speed rpm	Flocc. time min.	% Turbidity	Removal S.S.
1	600	0.77	160	21.20	34.6	38.1
2	700	0.77	180	27.30	49.5	65.7
3	800	0.78	180	33.50	48.0	7.2
4	880	0.78	200	39.60	44.0	40.7
5	700	1.50	180	27.30	47.0	88.9
6	700	2.25	180	27.30	41.7	95.7

Although more tests along the Path of Steepest Ascent may give better results, it was not the objective of the pilot study to obtain optimal conditions for the coagulation process. The results obtained were already equal to, or better than that of the plant's readings. The removal of suspended solids had reached 95.7%, and further removal was not expected.

Using the mixing conditions for Trial no. 6, the effect of an increase in settling time is shown in Table 7.

Table 7. Turbidity Reduction at Different Settling Times

Settling Time (min)	Turbidity Run #1	NTU Run #2
Initial reading	10.0	45.0
30	5.1	16.0
45	4.2	10.0
60	3.9	8.9
75	-	8.5
80	-	7.0

The final conditions chosen for use in the pilot plant batch coagulation-flocculation process were

Rapid-mix speed of 700 rpm

Rapid-mix time of 2.25 min

flocculation speed of 180 rpm

Flocculation time of 27.30 min

Settling time of 45 minutes

The effectiveness of the coagulation process during runs in the pilot plant, in the months of June and August, 1983, is summarized in Table 8. In general, the turbidity and suspended solids removal were better than that was obtained in the main plant. The batch coagulation system, however, was not effective when the raw water turbidity level was below 10 NTU.

Table 8. Pilot Plant Turbidity and Suspended Solids reductions

TURBIDITY, NTU					SUSPENDED SOLIDS, mg/L		
Raw	Pilot Plant Post Flocc.	Reduction (%)	Main Clarifier	Plant Stilling basin	Pilot Plant Raw	Post Flocc.	Reduction (%)
77	17	80	14	11	147	28	81
99	26	38	44	7.5	126	35	72
36	14	61	NA	NA	60	23	62
19	9.5	50	6.0	3.5	37	8.5	77
140	12	91	NA	NA	392	15	96
108	13	88	47	15	354	34	90
130	10	92	22	13	387	20	95
115	11	90	18	10	361	17	95
36	8.5	76	-	-	102	10	90
87	25	71	-	-	140	34	76
38	15	61	-	-	89	26	71
42	16	63	-	-	129	29	78
19	11	42	-	-	48	13	73
26	14	48	-	-	94	31	67
20	12	39	-	-	59	33	44
20	9.9	49	-	-	49	19	61
4.7	5.1	inc	-	-	-	-	--
2.6	4.6	inc	-	-	7	5	29
2.7	4.4	inc	-	-	23	26	inc
2.7	3.5	inc	-	-	1.5	0.5	67
2.4	4.0	inc	-	-	0.0	0.0	0.0
2.5	3.4	inc	-	-	17	16	3.0
3.2	3.9	inc	-	-	1.0	1.0	0.0
3.0	3.1	inc	-	-	8.0	4.0	50
4.7	4.5	4.3	-	-	6.5	6.0	7.7
3.1	3.5	inc	-	-	5.5	2.5	55
4.3	4.2	2.3	-	-	7.5	2.5	67
4.1	4.2	inc	-	-	11	5.5	48

inc : increase
NA : data not available

B. Ethylbenzene Removal

Coagulation-Flocculation

Although the major emphasis of the study was on the removal of the surrogate chemicals by the oxidants and GAC, some initial tests were conducted in order to determine the effect of the coagulation-flocculation process on ethylbenzene removal.

A known concentration of ethylbenzene was added to the raw water in the coagulation-flocculation tank. The chemical, along with the turbidity and suspended solid readings, was monitored before and after alum addition. The results were tabulated in Table 9.

It appeared that alum coagulation and settling was not effective in the reduction of ethylbenzene in the water, under the conditions tested. Accordingly, all further spiking was done in the storage tank, after the batch coagulation process in order to minimize volatilization when transferring water to the storage tank.

Table 9. Effect of Coagulation-Settling Process on Ethylbenzene

	Run # 1	# 2	# 3
Alum conc., mg/L	70	70	35
Ethylbenzene conc., ug/L			
Raw	125	128	126
after settling	122	143	142
Turbidity, NTU			
Raw	-	37.5	19.0
after settling	-	14.5	11.0
Suspended Solids, mg/L			
Raw	-	88.5	48.0
after settling	-	25.5	13.0

Removal by Oxidants and GAC

The data for ethylbenzene removal by oxidants and GAC are given in Table 10. Each line represents one day's run. All the parameters and data are presented in Appendix VII. To determine where statistically significant reductions occurred, the data were analyzed by the unequal sample size Analysis of Variance Method (ANOVA) described by Lindman (1974). Where significant differences among treatments occurred, samples with significant difference were determined using the Tukey's Least Significant Difference Test

(Snedecor, 1956, Larmond, 1977).

Sample calculations for ANOVA are given in Table 11 through 15.

Table 11 shows the ANOVA calculation comparing ethylbenzene readings after treatment with the two oxidants at 0.5 mg/L dosage and 30 min contact time, and the initial readings in the storage tank.

Table 12 shows similar calculation but with the oxidants being applied at 60 min contact time.

Table 13 tests the interaction between oxidants and the contact time by combining the ANOVA calculation for the data in Table 10 and 11. No significant differences were detected.

Table 14 compares the effect of the oxidants at a dosage of 1.0 mg/L at 30 minutes contact time. Significant differences were detected. Tukey's Test (Table 15) showed that ozonation produced lower ethylbenzene readings than after treatment with chlorine dioxide and the initial storage tank readings.

All other ANOVA tables for the ethylbenzene study are given in Appendix III

Tables III-1 through III-11 - compare the effect of oxidation

Tables III-12 through III-26 - test the differences between GAC readings, with or without pre-oxidation, and the storage tank readings

Tables III-27 through III-33 - compare the GAC with the post-oxidation readings if oxidation by itself produced results significantly different from the storage tank readings

The results of the ANOVA tests on ethylbenzene removal in the pilot plant are summarized in Table 16.

Date	Oxidant Dosage/ contact time	Storage Water	Post ClO_2	ClO_2 - GAC	Post O_3	O_3 - GAC	GAC only	Carbon
D/M 1983	mg/L-min	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	
25/8	0.5/30	127	113	ND	125	11	18	A
24/8		125	163	<10	150	26	15	B
23/8	0.5/60	127	132	58	117	28	<10	A
15/8		126	81	ND	88	<10	-	A
31/8		123	50	15	81	15	27	B
17/8	1.0/30	125	136	46	67	<10	-	A
26/8		128	-	ND	51	<10	10	B
30/8		128	113	31	17	11	11	A
18/8	1.0/60	127	79	ND	41	<10	-	B
19/8		125	-	-	65	13	ND	A
19/8						15		B
29/8		125	154	11	68	<10	52	A
13/9	2.0/30	124	105	ND	<10	ND	60	B
12/9		124	140	52	<10	<10	<10	A
8/9		128	131	43	-		29	B
9/9		126	-	-	25	<10	91	B
7/12	1.0/30	123	109	<10	-		ND	A
6/12		124	96	-	93	<10	<10	B
8/12		124	-	-	110	<10	<10	A
14/12	1.0/60	124	86	<10	-	<10	<10	B
15/12		126	133	<10	132	<10	-	A
16/12	2.0/60	148	127	12	33		95	B
17/12		125	96	<10	46	<10		A

ND : Not detected (5.0 ug/L is used in calculation)
Carbon A : Calgon
Carbon B : Pacific Carbon (Pacarb 800)

Table 10: Ethylbenzene Reductions by Oxidants and GAC

Storage	ClO_2	Ozone	Sum
127.2	113.4	125.4	366.0
125.1	163.2	149.5	437.8
252.3	276.6	274.9	803.8

	RS	SS	df	MS	F Value
mean (m)		107682.41			
between (b)	107866.43	184.02	2	92.01	0.18
within (w)		1532.63	3	510.88	
total (t)	109399.06	1716.65	5		

$F_{2,3} = 9.55$, with no significant difference at the 5% level

Table 11. Ethylbenzene Removal by 0.5 mg/L ClO_2 and Ozone at 30 minutes contact time

Storage	ClO_2	Ozone	Sum
127.3	131.5	117.2	376.0
125.6	80.8	87.8	294.2
123.4	50.4	81.3	255.1
376.3	262.7	286.3	925.3

	RS	SS	df	MS	F
m		95131.12			
b	97526.89	2395.77	2	1197.89	1.75
w		4096.74	6	682.79	
t	101623.63	6492.51	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table 12. Ethylbenzene Removal by 0.5 mg/L ClO_2 and Ozone at 60 minutes contact time

	Storage	ClO_2	Ozone	Sum
30 min	127.2	113.4	125.4	
	125.1	163.2	149.5	
Sum	252.3	276.6	274.9	Sum=803.8
ave.	126.15	138.3	137.45	Ave.=133.97
60 min	127.3	131.5	117.2	
	125.6	80.8	87.8	
	123.4	50.4	81.3	
Sum	376.3	262.7	286.3	Sum=925.3
ave.	125.43	87.57	95.43	ave.=102.81
Sum	628.6	539.3	561.2	Sum=1729.1
ave.	125.79	112.94	116.44	ave.=118.39

	RS	SS	df	MS	F
m		201833.17			
a	205328.57	3495.40	1	3495.40	8.83
b	202256.84	423.67	2	211.83	0.53
ab	207459.10	1706.86	2	853.43	2.16
w		3563.59	9	395.95	
t	211022.69	9189.52	14		

For a, $F_{1,9} = 5.12$, with significant difference at the 5% level
For b and ab, $F_{2,9} = 4.26$, with no significant difference at the 5% level

Table 13. Ethylbenzene Removal by 0.5 mg/L ClO_2 and Ozone at 30 and 60 minutes Contact Time

Storage	ClO_2	Ozone	Sum
125.1	138.0	66.6	
127.8	-	51.4	
128.3	113.3	17.1	
381.2	251.5	135.1	767.8

	RS	SS	df	MS	F
m		73689.61			
b	86147.94	12458.33	2	6229.17	20.14
w		1546.62	5	309.32	
t	87694.56	14004.95	7		

$F_{2,5} = 5.79$, with significant difference at the 5% level

Table 14. Ethylbenzene Removal by 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table 15. Tukey's Test for Data in Table 14.

For 3 treatment and df(W)=5, Student t at 5%=4.54
Standard Error = SQR (309.32 / 3) = 10.15
Least Significant Difference = 10.15 x 4.54 = 46.10
Any two sample means that differ by 46.10 or more are significantly different at the 5% level

127.75 - 127.07 = 0.68
127.75 - 45.03 = 82.72
127.07 - 45.03 = 82.04

Conclusion : Ozone readings are significantly different from the storage tank and ClO_2 readings

Table 16. Summary of Ethylbenzene Removal in Pilot Plant

Dosage	30 minute Contact time		60 minute Contact time	
	Post Oxidation	GAC	Post Oxidation	GAC
ClO_2 :				
0.5 mg/L	NSD	SD, a	NSD	SD
1.0 mg/L	NSD	SD	NSD	SD
2.0 mg/L	NSD	SD, a	-	-
1.0 mg/L*	NSD	SD	NSD	SD
2.0 mg/L*	-	-	NSD	SD
Ozone :				
0.5 mg/L	NSD	SD	NSD	SD
1.0 mg/L	SD	SD, c	SD	SD, b
2.0 mg/L	SD	SD, c	-	-
1.0 mg/L*	NSD	SD	NSD	SD
2.0 mg/L*	-	-	SD	SD, c

NSD : with no significant difference from the storage tank at the 5% level
SD : with significant difference at the 5% level
a : ClO_2-GAC were more effective than the corresponding Ozone-GAC
b : GAC readings are significantly different from the post-oxidation readings
c : GAC readings are not significantly different from the post-oxidation readings
* : Additional tests conducted in December 1983

Bench studies were also conducted to compare the reactions of the surrogate chemical in bench and pilot scale. An oxidant concentration of 2.0 mg/L were mixed with 125 ug/L ethylbenzene in volumetric flasks. Samples were withdrawn at half-an-hour intervals for GC analyses. However, the bench study results were inconclusive in regard to the decrease in ethylbenzene levels with time. This might be due to the limited number of tests conducted with the time restraint, as well as the difficulties in dispensing an accurate dosage of ozone. To give 2.0 mg/L of ozone, the ozone gas outlet was submerged in the testing flasks for only two to five seconds. A error of one second could lead to an error of 0.5 mg/L. A more accurate method for dispensing small quantity of ozone at bench scale must therefore be available before valid results can be obtained. No by-products were found in the bench study.

In the pilot plant, ozone began to exert its effect at 1.0 mg/L, giving approximately 55 to 65% reduction from the levels in the storage tank. Its effectiveness was increased to 87% at a dosage of 2.0 mg/L. Chlorine dioxide was not effective in reducing the ethylbenzene concentration at the dosages tested (0.5 to 2.0 mg/L). Based on these results, ozone can be considered the better oxidant for ethylberizene reduction. The changes in the oxidant contact time had no effect on ethylbenzene removal. The long contact time used was to simulate the time required for the water to pass through the settling basin in the main plant. Ozone and chlorine dioxide are both highly reactive oxidants, and any significant reduction of ethylbenzene would have occurred in the first few minutes of contact. If the contact time parameters were set at three to five minutes, there may be significant differences between the readings.

All GAC systems, with or without any pre-oxidation treatment, were equally effective in the reduction of ethylbenzene, producing reductions ranging from 70 to 100%. The changes in oxidant dosage did not alter the performance of the GAC columns and the ethylbenzene reduction was the same for both types of carbon. ClO_2-GAC was more effective than the O_3-GAC and GAC-only systems at an oxidant dosage of 0.5 mg/L - 30 minute contact time and 2.0 mg/L - 60 minute contact time.

Levels below the detection limits were obtained in early runs, indicating the effectiveness of the fresh carbon. Since the first sampling port was used, the effective bed depth was only 200 mm (8"). Not surprisingly, breakthrough occurred in later runs. It should be emphasized that the experiments were not designed to obtain quantitative GAC loading data. Rather, they were intended to give a qualitative indication of the GAC performance, as a prelude to later detailed investigations.

C. TOC Reduction

TOC data were obtained for all pilot plant runs.

The effect of the oxidants and the GAC, with or without pre-oxidation treatment, was analyzed by ANOVA methods similar to those used for the ethylbenzene. The results (Table IV-1 through IV-22) are listed in Appendix IV and summarized in Table 17 and 18. Tables IV-1 through IV-8 compare the effect of oxidation, and Tables IV-9 through IV-22 test the differences between the GAC readings, with or without pre-oxidation, and the

storage tank readings.

No change in the TOC levels was observed for either oxidant at various concentrations and contact times. This was as expected, since complete conversion of ethylbenzene to carbon dioxide was not possible under the conditions tested. This is because TOC is only a gross measurement of the surrogate. The concentration of the ethylbenzene is very small when compared to the overall TOC present.

In general, all the GAC columns, with or without any pre-oxidation treatment, were effective in lowering the TOC levels. The only exceptions were ClO_2-GAC at 0.5 mg/L - 30 minute contact time, and Ozone-GAC at 0.5 mg/L - 60 minute contact time. A lowering of the TOC levels by GAC would be expected for fresh carbon. The changes in TOC levels were the same for both types of GAC.

Date	Oxidant Dosage/ contact time mg/L-min	Storage Water mg/L	Post ClO_2 mg/L	ClO_2 GAC mg/L	Post O_3 mg/L	O_3-GAC mg/L	GAC only mg/L	Carbon
25/8	0.5/30	3.18	3.28	2.02	3.15	2.03	1.85	A
24/8		3.34	3.41	1.80	3.18	1.63	1.89	B
22/8		3.99	3.73	3.12	3.68	1.94	-	B
23/8	0.5/60	3.24	3.22	2.01	3.23	2.92	1.73	A
15/8		2.83	2.93	0.70	2.84	2.46	-	A
31/8		2.85	2.68	1.31	3.29	-	1.39	B
17/8	1.0/30	3.70	3.71	2.23	3.62	2.21	-	A
26/8		3.16	3.11	1.33	3.55	1.66	1.67	B
30/8		3.28	2.80	1.61	3.01	1.73	1.16	A
18/8	1.0/60	4.54	3.55	1.94	3.71	1.78	-	B
19/8		3.64	-	-	3.55	2.58	2.06	A
19/8						1.58		B
29/8		4.42	2.92	1.58	3.13	1.47	1.77	A
13/9	2.0/30		3.47	3.87	1.88	3.74	2.84	B
12/9		3.31	3.35	1.29	3.51	1.71	2.56	A
8/9		2.76	3.26	1.43	-	-	1.47	B
9/9		3.40	-	-	3.48	1.85	1.88	B
14/9		2.43	-	2.38	-	-	-	-

Carbon A : Calgon
Carbon B : Pacific Carbon (Pacarb 800)

Table 17. TOC Reductions by Oxidants and GAC

Table 18. Summary of TOC Reduction

Dosage	30 minute Contact time Post Oxidation	GAC	60 minute Contact time Post Oxidation	GAC
ClO_2 :				
0.5 mg/L	NSD	NSD	NSD	SD
1.0 mg/L	NSD	SD	NSD	SD
2.0 mg/L	NSD	SD	-	-
Ozone :				
0.5 mg/L	NSD	SD	NSD	NSD
1.0 mg/L	NSD	SD	NSD	SD
2.0 mg/L	NSD	SD	-	-

Legend as per Table 16

D. Colour Reduction

The changes in colour during the pilot plant tests were analyzed. The results are listed in Appendix V, and summarized in Table 19 and 20.

Tables V-1 through V-11 compare the effect of oxidation

Tables V-12 through V-22 test the differences between GAC readings, with or without pre-oxidation, and the storage tank readings

Table V-23 and V-24 show ANOVA testing to compare the post-oxidation and the GAC readings, when oxidation by itself produced results significantly different from the storage tank readings

Contradictory results were obtained regarding the effectiveness of the oxidants and GAC on colour removal. There was no colour reduction due to the oxidants at 0.5 mg/L - 60 minute contact time and 1.0 and 2.0 mg/L, both at 30 minute contact time. Ozonation, however, was effective at 0.5 mg/L - 30 minute contact time and 1.0 mg/L - 60 minute contact time.

GAC was only effective at 0.5 and 1.0 mg/L at 30 minute contact time. It could suggest that the prolonged contact time in oxidation treatment may have decreased the colour removal capacity in the GAC systems. However, with the limited data available, further research is necessary in order to conclude the reduction of colour by the oxidants or the GAC systems. Base on the data available, the inconsistency could be due to the changes in initial colour levels. When there was a high raw water colour level, such as 7 TCU, the oxidants were able to further reduce the colour levels. However, if the initial readings were already low, no further reduction could be observed. The differences may therefore reflect the ability of the oxidants to further reduce the low level of colour in the water. A TCU of 7 is a very high reading for a raw water sample.

Date	Oxidant Dosage/ contact time mg/L-min	Storage Water TCU	Post ClO_2 TCU	ClO_2 GAC TCU	Post O_3 TCU	O_3-GAC TCU	GAC only TCU	Carbon
25/8	0.5/30	7	2	1	1	1	1	A
24/8		3	3	1	2	<1	<1	B
22/8		5	4	2	1	1	-	B
23/8	0.5/60	3	1	1	2	1	1	A
15/8		5	3	1	2	1	-	A
31/8		2	1	0	1	-	1	B
17/8	1.0/30	3	1	1	1	1	-	A
26/8		2	1	1	1	1	1	B
30/8		4	2	1	2	1	1	A
18/8	1.0/60	4	2	1	1	1	-	B
19/8		4	-	-	2	1	1	A
19/8						3		B
29/8		4	3	1	1	1	1	A
13/9	2.0/30	4	2	-	1	1	1	B
12/9		2	1	0.5	0.5	0.5	1	A
8/9		3	2	0	-	-	1	B
9/9		1	-	-	1	1	3	B
14/9		4	4	-	3	-	-	-

Carbon A : Calgon
Carbon B : Pacific Carbon (Pacarb 800)

Table 19. Colour Reductions by Oxidants and GAC

Table 20. Summary of Colour Reductions

Dosage	30 minute Contact time Post Oxidation	GAC	60 minute Contact time Post Oxidation	GAC
ClO_2 :				
0.5 mg/L	NSD	SD	NSD	NSD
1.0 mg/L	NSD	SD	SD	NSD
2.0 mg/L	NSD	NSD	-	-
Ozone :				
0.5 mg/L	SD	SD, c	NSD	NSD
1.0 mg/L	NSD	SD	SD	NSD
2.0 mg/L	NSD	NSD	-	-

Legend as per Table 16

E. Turbidity Reduction

The changes in turbidity levels during pilot plant testing were analyzed and the results are listed in Appendix VI, and summarized in Table 21 and 22.

Tables VI-1 through VI-7 compare the effect of oxidation.

Tables VI-8 through VI-25 test the differences between GAC readings, with or without pre-oxidation, and the storage tank readings

It was not expected that the oxidants would have any effect on the turbidity reduction. Any changes could be contributed to the settling of suspended solids in the contact and retention tanks. Statistical analyses of the data showed that there were no significant changes in the turbidity levels from those in the storage tank at any oxidant dosages or contact time.

All GAC systems, with or without any pre-oxidation treatment, were effective in reducing the turbidity levels. A simple filtration mechanism would be expected. Further analyses, however, showed that turbidity reduction were significantly less at an oxidant dosage of 2.0 mg/L and for GAC-only systems run #5. These tests were conducted at the same time after all the other studies. A simple explanation would be that the carbon columns were exhausted with regard to turbidity removal.

Date	Oxidant Dosage/ contact time mg/L-min	Storage Water NTU	Post ClO_2 NTU	ClO_2 GAC NTU	Post O_3 NTU	O_3-GAC NTU	GAC only NTU	Carbon
25/8	0.5/30	3.0	2.9	0.31	3.1	0.31	0.51	A
24/8		4.4	3.6	1.5	3.4	0.45	0.70	B
22/8		4.6	3.9	2.1	3.7	1.6	-	B
23/8	0.5/60	3.0	2.5	0.55	3.0	0.36	0.85	A
15/8		4.6	3.4	0.51	3.5	0.55	-	A
31/8		3.3	2.5	0.87	2.4	--	0.55	B
17/8	1.0/30	3.5	3.4	0.51	3.0	0.49	-	A
26/8		3.5	3.4	1.0	3.4	1.6	0.64	B
30/8		4.2	3.9	0.43	3.7	0.31	0.35	A
18/8	1.0/60	3.9	3.1	1.94	3.1	1.78	-	B
19/8		3.4	-	-	3.0	0.50	1.0	A
19/8						0.84		B
29/8		4.2	3.4	0.23	3.3	0.21	0.49	A
13/9	2.0/30	35	32	4.0	36	3.0	3.0	B
12/9		31	30	4.0	30	3.0	3.0	A
8/9		26	24	5.0	-	-	6.0	B
9/9		66	-	-	55	5.0	8.0	B
14/9		27	25	-	26	-	-	-

Carbon A : Calgon
Carbon B : Pacific Carbon (Pacarb 800)

Table 21. Turbidity Reductions by Oxidants and GAC

Table 22. Summary of Turdibity Reductions

Dosage	30 minute Contact Time		60 minute Contact Time	
	Post Oxidation	GAC	Post Oxidation	GAC
ClO_2 :				
0.5 mg/L	NSD	SD	NSD	SD
1.0 mg/L	NSD	SD	NSD	SD
2.0 mg/L	NSD	SD	-	-
Ozone :				
0.5 mg/L	NSD	SD	NSD	SD
1.0 mg/L	NSD	SD	NSD	SD
2.0 mg/L	NSD	SD	-	-

Legend as per Table 16

IX. CONCLUSIONS

The abatement of taste and odour in water supplies is a very complex problem because of the large number of variables involved. Although there are different proven chemical and / or physical methods, a successful program of taste and odour control must include :

1. identification of the source(s) and causes(s);
2. identification of the chemical(s) involved;
3. review of the state-of-art technology available for the removal of the chemical(s) for the specific water supply system;
4. understanding of the water chemistry involved; and
5. continuous monitoring of the results and the possible formation of any reaction by-products.

GC / MS analysis of the City of Edmonton's raw and treated water during a period of spring runoff had identified a complex array of chemicals in the raw and treated water; the most prominent ones being the paraffins, hydrocarbon, and aromatics. However, most of the chemicals are not present in any significant concentration, and only a few are of any health concern. Trihalomethane and its formation is not a problem for the City water.

Treatment methods examined in the literature review included the use of ozone, chlorine dioxide, powdered granular and biological activated carbon (BAC), potassium permanganate, copper sulphate, coagulation, and hydrogen peroxide. Ozonation, chlorine dioxide and the use of granular activated carbon appeared to have the greatest potential in the abatement of the problem in Edmonton water.

Chlorine dioxide and ozone are, in many ways, more effective disinfecting agents than chlorine. However, the health effects of their reaction products, particularly the chlorite from chlorine dioxide, and oxidized organics from ozone, are not well established. Based on the literature review, the uncertainties are usually outweighted by the beneficial effects of the two oxidants.

A pilot plant was set up in the Rossdale Water Treatment Plant, testing the use of ozone, and chlorine dioxide, with or without granular activated carbon. In order to optimize the pilot plant system so the water tested was comparable to the main Plant's, a coagulation study was conducted, using the Path of Steepest Ascent method. The effects

of coagulation on taste and odour removal were also studied. Surrogate chemical(s) were used in order to give a more controlled environment. Parameters monitored included GC, TOC, colour, turbidity, suspended solids, pH and temperature. Results were analyzed by the unequal sample size ANOVA method.

Results obtained in the pilot study showed that ozone provided a better reduction than chlorine dioxide for ethylbenzene, a compound of known health and organoleptic concern. Under the conditions tested, ozonation provided effective (87%) ethylbenzene removal, at a dosage of 2.0 mg/L. The removal was only 55-65% at 1.0 mg/L, but a continuous increase in effectiveness with increased dosage was observed. The concentration of ethylbenzene used was a factor of ten higher than normally would be found in the water. It is therefore possible that in usual plant operation, 1.0 mg/L ozone may be sufficient for the removal of ethylbenzene.

Chlorine dioxide was less effective at the dosages tested (20% removal). This finding was not unexpected based on the chemistry of chlorine dioxide. The change in contact time had little effect on the oxidation results. This is because any chemical reactions with ethylbenzene will have taken place within the first few minutes. The long contact time was necessary to simulate actual plant conditions. The difficulties in producing an accurate amount of ozone for bench testing had hindered the study of by-product(s) formation.

GAC with or without pre-oxidation treatment, was able to reduce the ethylbenzene concentration up to 100%. The beneficial effect of the BAC system was not observed, possibly due to the short testing period. There were no differences between the two types of carbon tested. Coagulation was also not effective in the reduction of ethylbenzene concentration.

The effects of the oxidants on TOC and turbidity were as expected. The two oxidants were not effective in lowering the levels, but GAC was. The results for colour reduction were very inconsistent, perhaps as a result of fluctuating initial raw water colour levels. No interaction between the various parameters was observed.

The oxidative power of ozone, and the ability of GAC to adsorb organics were clearly demonstrated in this pilot study. Since ethylbenzene is one of the more prominent chemicals of health and organoleptic concern found in the raw and treated water, the use

of ozone and GAC should be considered as potential treatment methods. There is, however, no simple solution because of the complex river matrix. The results from the testing of other families of chemicals must also be considered before a decision can be made on the application of an advanced treatment system in the plant.

This pilot study served only as the first step in the abatement of the taste and odour problem in the City of Edmonton. The problem, however, is not resolved and further research is necessary to give a better understanding of various treatment aspects, which include :

1. expansion of the surrogate chemical testing to various families of chemicals found in the water;
2. testing of the chemicals individually and as a complex mixture;
3. monitoring and testing of possible by-product(s) formed from the use of ozone and chlorine dioxide with the river water;
4. evaluation of the disinfection ability of the oxidants;
5. study of the effectiveness of the oxidants at a concentration normally used in the plant;
6. addition of humic materials for artificial colour runs;
7. conduction of continuous GAC runs;
8. monitoring of GAC columns, including the growth of bacteria, and the possible generation of toxic compounds in the columns; and the
9. understanding of the distribution of the adsorbed compound(s) within the carbon columns.

Improvements to the pilot plant that may be necessary to obatin these results include :

1. modification of the chlorine dioxide retention chamber so the contactors are identical for both oxidants;
2. the need for a more accurate dispensing method for ozone at low concentration for bench studies; and
3. the use of more sensitive instrumentation so surrogate chemicals can be added at a level close to that found in the water, giving a better indication of the effectiveness of the oxidants and GAC at a much lower concentration.

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APPENDIX I

TASTES AND ODOURS TERMINOLOGY AND UNIT OF MEASUREMENT

Acceptability (Hedonic Tone) - Pleasant or unpleasant and to what degree.

Detectability - Concentration of a substance at which its odourant or taste is detectable.

Detection Threshold - The minimum physical intensity detected by a subject when he is not required to identify the stimuli, but just detect the existence of the stimuli (ASTM, 1978b).

Difference Threshold - The smallest physical difference between two stimuli which can be identified as sensory different (the smallest change in concentration of a substances required to give a perceptible change) (ASTM, 1978b).

Hedonic index - A combination of both odour classification and Odour Threshold. The heometric value of OT is assigned to one scale and a numerical value of the quality (characterization) to another scale. The product of these is the index (hedonic) for rating odour in water.

Intensity - Strength of the taste and odour.

Odour Dectection Threshold - Concentration at which a subject gives a positive reponse in 50% of the cases in which the stimulus is presented to him. The Odour Threshlod Concentration (OTC) is the concentration at which for 50% of subjects the Odour Detection Threshold is trespassed (Zoeteman, 1980).

Odour Intensity Index (OII) - The number of times the sample had to be diluted in half to reach the threshold level. Used for more intensely contaminated samples (Table I-1) (Barth, 1973; Baker, 1966).

Odour Number (ON) - The number of dilutions required to reach ODT. It is a measurement of Odour Intensity (Zoeteman, 1980).

Quality of character - Degree of similarity to various other taste and odour.

Recognition Threshold - The minimum physical intensity detected by a subject where he is required to identify the stimuli in some manner (Lowest concentration at which a substance is correctly identified) (ASTM 1978b).

Taste Number - The number of subsequent halvings of the concentration of a sample by tasteless water before the sample is judged to have no taste (Water Research Centre, 1977).

Terminal Threshold - Concentration of a substance above which changes in concentration are not perceptible (ASTM, 1978b).

Threshold Concentration - Lowest concentration in mg/L giving perceptible odour and/or taste (McKee and Wolf, 1963).

Threshold Odour or Odour Threshold or Threshold Odour Number (TO or TON)- As an odourous gas or vapour is diluted with air or water, a point is finally reached when, on further dilution, the odour can no longer be detected. The minimun concentration is called the Threshold Odour (Table I-1) (Fiero, 1958; Dague, 1972).

Table I-1. Odour Dilution and Measurements

Dilution	Volume Transferred to Flask, mL	TON (Dilution Factor)	OII
Original sample	200	1	0
	100	2	1
	50	4	2
	25	8	3
	12.5	16	4
A	50	32	5
	25	64	6
	12.5	128	7
B	50	256	8
	25	512	9
	12.5	1,024	10
C	50	2,050	11
	25	4,100	12
	12.5	8,200	13
D	50	16,400	14
	25	32,800	15
	12.5	65,500	16

Note : A = 25 mL of original sample diluted to 200 mL;
B = 25 mL of dilution A diluted to 200 mL;
C = 25 mL of dilution B diluted to 200 mL;
D = 25 mL of dilution C diluted to 200 mL.
Panel members were periodically given odour-free blanks to check their sensitivity.
Volume in odour flasks is made up to 200 ml with odour-free water.
(Dolan, 1975). TON= 2^{011}

APPENDIX II

COMPARISON OF OXIDATION OF ORGANIC COMPOUNDS WITH OZONE, CHLORINE DIOXIDE, AND CHLORINE (Miller *et al.*, 1978)

Phenol:

Ozone

Intermediates: polyhydroxy aromatics and quinones. Then ring ruptured, non-halogenated difunctional products (alcohol-aldehyde, aldehyde-acid; alcohol-acid). End-products: oxalic acid, carbon dioxide and water.

Chlorine Dioxide

Same as for Ozone plus chlorinated phenols and chloroquinones. Upon ring rupture, the same non-chlorinated products as for ozone are obtained, plus some chlorinated aliphatics.

Chlorine

Chlorophenols plus ring ruptured products (presumably chlorinated); also non-chlorinated products (aromatic and ring-ruptured).

Cresols and Xylenols

Ozone

Same products as from phenol, plus methyl-substituted compounds (salicyclic acid as aromatic intermediate, propionic and acetic acids after ring rupture). Acetic acid, oxalic acid, carbon dioxide and water as end products.

Chlorine

Probably chlorinated aromatics, then ring rupture.

Chlorinated phenols

Ozone

Chloride ion plus same products as from phenol. Oxalic acid and carbon dioxide as end products.

Chlorine Dioxide

Chloroquinones plus ring ruptured, halogenated and non-halogenated aliphatics.

Chlorine

Probably more highly chlorinated phenols, then ring rupture.

Chlorinated Benzenes

Ozone

Chlorophenols, then chloride ion and non-chlorinated, ring ruptured products, as with chlorophenols, plus some chlorotartaric acid.

Chlorine

Probably more highly chlorinated products.

Miscellaneous Aromatics

Ozone

Nitro, amino and sulfonic acid groups are cleaved, but more slowly than chlorine. Oxalic acids and carbon dioxide as end products.

Chlorine Dioxide

Benzoic, phenylsulfonic and cinnamic acids are not reactive to chlorine dioxide. Nitro groups are split off during oxidation.

Polycyclic Aromatics

Ozone

Undergo ring rupture producing polycarboxylic aromatics, which become increasing resistant to further oxidation.

Chlorine Dioxide
Produces polycyclic non-halogenated quinones plus chlorinated polycyclic aromatics. Eventual ring-rupture likely, but at slower rate than with ozone.
Chlorine
Probably same products as with chlorine dioxide

Diphenylhydrazine or Diphenylamine
Ozone
Hydroxylamines and ring hydroxylated diphenylamine.
Chlorine Dioxide
Ring-chlorinated, ring-hydroxylated and ring-chlorinated plus hydroxylated diphenylamine.

Nitrogen Heterocycles
Ozone
Ring rupture to amino acids, then further degradation to aliphatic end products
Chlorine Dioxide
Thiamine stable. Pyrimidine and indole rings apparently stable. Substituents oxidize, but do not chlorinate.

Unsaturated aliphatics
Ozone
Cleavage of double bond to aldehydes, ketones and acids. Possible formation of epoxides
Chlorine Dioxide
Dichloro compounds, chloroketones, chlorohydrins, then epoxides.
Chlorine
Dichloro compounds, chlorohydrins, then epoxides under alkaline conditions.

Primary Aliphatic Alcohols
Ozone
Yield aldehydes, then acids, then carbon dioxide. Ethanol forms a dihydroperoxide with mutagenic properties under stringent conditions.
Chlorine Dioxide
Yield acids which are stable to further oxidation. Unsaturated acids (crotonic, maleic and fumaric) are stable to chlorine dioxide .

Secondary Alcohols
Ozone
Yield ketones, then fragmented acids, then carbon dioxide.
Chlorine Dioxide
Yield ketones, then acetic acid, which is stable.

Primary Aliphatic Amines
Chlorine Dioxide
No reaction

Secondary Aliphatic Amines
Ozone
Aldoximes plus other N- containing compounds, not nitrosamines.
Chlorine Dioxide
Very slow reaction

Tertiary Aliphatic Amines
Chlorine Dioxide
Secondary amine plus aldehyde.

Chloroform
Ozone
No reaction except in presence of UV
Chlorine Dioxide
Probably no reaction
Chlorine
No reaction.

Humic Materials
Ozone
Slowly reactive, producing phenols, ozone resistant acids (increasing COD) and carbon dioxide.
Chlorine Dioxide
Slowly reactive, producing phenols and increasing COD
Chlorine
Trihalomethanes

Sugars, Carbohydrates
Chlorine Dioxide
Ring substituents oxidize without ring rupture until excess chlorine dioxide employed.

Trihalomethane Precursors
Ozone
1) Ozone plus rapid chlorination: 65% lowering of THM
2) Ozone plus chlorination after 24 hours, no effect on THM yield.
Chlorine Dioxide
No THM produced from pure chlorine dioxide (containing no free chlorine).
Chlorine
Trihalomethanes.

Phosalone, Aldrin
Ozone
Readily oxidized to destruction.

2,4,5-T
Ozone
Ring rupture to oxalic acid plus carbon dioxide and chloride ion.

Parathion, Malathion
Ozone
Produces oxons, then degradation products.

Dieldrin, Chlordane, Lindane, DDT, PCBs, PCP, Endosulfan
Ozone
Only slightly reactive with ozone, but will oxidize with ozone/UV.

APPENDIX III

ANOVA TABLES FOR ETHYLBEZENE STUDY

Storage	ClO_2	Ozone	Sum
127.2	113.4	125.4	366.0
125.1	163.2	149.5	437.8
252.3	276.6	274.9	803.8

	RS	SS	df	MS	F
m		107682.41			
b	107866.43	184.02	2	92.01	0.18
w		1532.63	3	510.88	
t	109399.06	1716.65	5		

$F_{2,3} = 9.55$, with no significant difference at the 5% level

Table III-1. Ethylbenzene Removal by 0.5 mg/L ClO_2 and Ozone at 30 minutes contact time

Storage	ClO_2	Ozone	Sum
127.3	131.5	117.2	376.0
125.6	80.8	87.8	294.2
123.4	50.4	81.3	255.1
376.3	262.7	286.3	925.3

	RS	SS	df	MS	F
m		95131.12			
b	97526.89	2395.77	2	1197.89	1.75
w		4096.74	6	682.79	
t	101623.63	6492.51	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table III-2. Ethylbenzene Removal by 0.5 mg/L ClO_2 and Ozone at 60 minutes contact time

	Storage	ClO_2	Ozone	Sum
30 min	127.2	113.4	125.4	
	125.1	163.2	149.5	
	-	-	-	
Sum	252.3	276.6	274.9	Sum=803.8
ave.	126.15	138.3	137.45	Ave.=133.97
60 min	127.3	131.5	117.2	
	125.6	80.8	87.8	
	123.4	50.4	81.3	
Sum	376.3	262.7	286.3	Sum=925.3
ave.	125.43	87.57	95.43	ave.=102.81
Sum	628.6	539.3	561.2	Sum=1729.1
ave.	125.79	112.94	116.44	ave.=118.39

	RS	SS	df	MS	F
m		201833.17			
a	205328.57	3495.40	1	3495.40	8.83
b	202256.84	423.67	2	211.83	0.53
ab	207459.10	1706.86	2	853.43	2.16
w		3563.59	9	395.95	
t	211022.69	9189.52	14		

For a, $F_{1,9} = 5.12$, with significant difference at the 5% level
For b and ab, $F_{2,9} = 4.26$, with no significant difference at the 5% level

Table III-3. Ethylbenzene Removal by 0.5 mg/L ClO_2 and Ozone at 30 and 60 minutes Contact Time

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Storage	ClO_2	Ozone	Sum
125.1	138.0	66.6	
127.8	-	51.4	
128.3	113.3	17.1	
381.2	251.5	135.1	767.8

	RS	SS	df	MS	F
m		73689.61			
b	86147.94	12458.33	2	6229.17	20.14
w		1546.62	5	309.32	
t	87694.56	14004.95	7		

$F_{2,5}$ = 5.79, with significant difference at the 5% level

Table III-4. Ethylbenzene Removal by 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table III-5. Tukey's Test for Data in Table III-4.

For 3 treatment and df(W)=5, Student t at 5%=4.54
Standard Error=SQR (309.32 / 3) = 10.15
Least Significant Difference = 10.15 x 4.54 = 46.10
Any two sample means that differ by 46.10 or more are are significantly different at the 5% level at the 5% level

127.75 - 127.07 = 0.68
127.75 - 45.03 = 82.72
127.07 - 45.03 = 82.04

Conclusion : Ozone readings are significantly different from the storage tank and ClO_2 readings

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Storage	ClO_2	Ozone	Sum
126.7	79.1	40.6	
125.1	-	65.3	
125.4	153.5	67.6	
377.2	232.6	173.5	783.3

	RS	SS	df	MS	F
m		76694.86			
b	84512.08	7817.22	2	3908.61	6.07
w		3217.25	5	643.45	
t	87729.33	11034.47	7		

$F_{2,5}$ = 5.79, with significant difference at the 5% level

Table III-6. Ethylbenzene Removal by 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

Table III-7. Tukey's Test for Data in Table III-6.

For 3 treatment and df(W)=5, Student t at 5% = 4.54
Standard Error=SQR (643.45 / 3) = 14.65
Least Significant Difference = 14.65 x 4.54 = 66.51
Any two sample means that differ by 66.51 or more are significantly different at the 5% level

125.73 - 116.30 = 9.43
125.73 - 57.83 = 67.90
116.30 - 57.89 = 58.47

Conclusion : Ozone readings are significantly different from the storage tank but not from the ClO_2 readings

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	Storage	ClO_2	Ozone	Sum
	125.1	138.0	66.6	
	127.8	-	51.4	
	128.3	113.3	17.1	
Sum	381.2	251.3	135.1	
ave.	127.07	125.65	45.03	99.26
	126.7	79.1	40.6	
	125.1	-	65.3	
	125.4	153.5	67.6	
Sum	377.2	232.6	173.5	
ave.	125.73	116.30	57.83	99.95
ave.	126.4	121.0	51.4	ave.=99.60

	RS	SS	df	MS	F
m		152968.87			
a	152970.76	1.89	1	1.89	0.0045
b	170946.97	17978.10	2	8989.05	21.62
ab	171265.93	317.07	2	158.54	0.38
w		4157.96	10	415.80	
t	175423.89	22455.02	15		

For a, $F_{1\ 10} = 4.96$, with no significant difference at the 5% level
For b and ab, $F_{2\ 10} = 4.10$, with significant difference at the 5% level for factor b

Table III-8. Ethylbenzene Removal by 1.0 mg/L ClO_2 and Ozone at 30 and 60 minutes contact time

Table III-9. Tukey's Test for data in Table III-8.

For 6 treatment and df(w)= 10, Student t at 5% = 4.91
Standard Error = SQR(4 15.80 / 3) = 11.77
Least Difference = 11.77 x 4.91 = 57.79
Any two sample means that differ by 57.79 or more are significantly different at the 5% level
Conclusion : Significant difference exist between post-ozone readings at both 30 and 60 minute level with post-ClO_2 treatment and storage tank readings.

Storage	ClO_2	Ozone	Sum
123.7	104.7	10.0	
123.7	140.0	10.0	
128.2	131.4	-	
126.3	-	25.3	
501.9	376.1	45.3	923.3

	RS	SS	df	MS	F
m		85248.29			
b	110810.34	25562.05	2	12781.02	105.49
w		848.11	7	121.16	
t	111658.45	26410.16	9		

$F_{2,7}$ = 4.74, with significant difference at the 5% level

Table III-10. Ethylbenzene Removal by 2.0 mg/L ClO_2 and 30 minute of contact time

Table III-11. Tukey's Test for Data in Table III-10.

For 3 treatment and df(W)= 7, Student t at 5% = 4.16
Standard Error = SQR (121.16 / 4) = 5.50
Least Significant Difference = 5.50 x 4.16 = 22.88
Any two sample means that differ by 22.88 or more are significantly different at the 5% level
Conclusion : Ozone readings are significantly different from the storage tank and ClO_2 readings; and
Chlorine Dioxide readings are significantly different from the storage tank readings

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Storage	ClO_2	Ozone	GAC Only	Sum
127.2	5.0	11.2	18.4	
125.1	10.0	26.2	14.6	
252.3	15.0	37.4	33.0	337.7

	RS	SS	df	MS	F
m		14225.16			
b	33184.03	18928.87	3	6309.62	187.73
w		134.42	4	33.61	
t	33318.45	19063.29	7		

$F_{3,4} = 6.59$, with significant difference at the 5% level

Table III-12. Ethylbenzene Removal by GAC after Pre-treatment with 0.5 mg/L ClO_2 and Ozone at 30 minute contact time

Table III-13. Tukey's Test for Data in Table III-12.

For 4 treatment and df(W) = 4, Student t at 5% = 5.76
Standard Error = SQR(33.61/2) = 4.10
Least Significant Difference = 5.76 x 4.10 = 16.81
Any two sample means that differ by 16.81 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly differnt from the storage tank readings.
The ClO_2-GAC readings are also significantly lower than the Ozone-GAC and the GAC-only readings.

Storage	ClO_2	Ozone	GAC Only	Sum
127.3	58.4	27.7	10.0	
125.6	5.0	10.0	-	
123.4	14.5	15.1	26.8	
376.3	77.9	52.8	36.8	543.8

	RS	SS	df	MS	F
m		26883.49			
b	50829.77	23946.28	3	7982.09	28.83
w		1937.79	7	276.83	
t	52767.56	25884.07	10		

$F_{3,7} = 4.35$, with significant difference at the 5% level

Table III-14. Ethylbenzene Removal by GAC after Treatment with 0.5 mg/L ClO_2 and Ozone at 60 minute contact time

Table III-15. Tukey's Test for Data in Table III-14.

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(276.83/3) = 9.60
Least Significant Difference = 9.60 x 4.68 = 44.93
Any two sample means that differ by 44.93 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly different from the storage tank readings

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Storage	ClO_2	Ozone	GAC Only	Sum
125.1	45.6	10.0		
127.8	5.0	10.0	10.0	
128.3	31.0	11.0	10.6	
381.2	81.6	31.0	20.6	514.4

	RS	SS	df	MS	F
m		24055.21			
b	51189.85	27134.64	3	9044.88	74.26
w		852.61	7	121.80	
t	52042.46	27987.25	10		

$F_{3,7} = 4.35$, with significant difference at the 5% level

Table III-16. Ethylbenzene Removal by GAC Columns after Treatment with 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table III-17. Tukey's Test for Data in Table III-16.

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(121.8/3) = 6.37
Least Significant Difference = 6.37 x 4.68 = 29.81
Any two sample means that differ by 29.81 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without pre-oxidation are significantly differnt from the storage tank readings

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Storage	ClO_2	Ozone	GAC Only	Sum
126.7	5.0	10.0	-	
125.1	-	13.3	5.0	
125.1	-	14.8	-	
125.4	10.5	10.0	52.0	
502.3	15.5	48.1	57.0	622.9

	RS	SS	df	MS	F
m		32333.70			
b	65399.35	33065.65	3	11021.88	77.42
w		1138.9	8	142.36	
t	66538.25	34204.55	11		

$F_{3,8} = 4.07$, with significant difference at the 5% level

Table III-18. Ethylbenzene Removal by GAC after Treatment with 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

Table III-19. Tukey's Test for Data in Table III-18.

For 4 treatment and df(W)=8, Student t at 5% = 4.53
Standard Error = SQR(142.36/4) = 5.97
Least Significant Difference = 5.97 x 4.53 = 27.04
Any two sample means that differ by 27.04 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without pre-oxidation are significantly differnt from the storage tank readings

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Storage	ClO_2	Ozone	GAC Only	Sum
123.7	5.0	5.0	60.4	
123.7	51.5	10.0	10.0	
128.2	42.5	-	29.4	
126.3	-	10.0	91.0	
501.9	99.0	25.0	190.8	816.7

	RS	SS	df	MS	F
m		51307.61			
b	75552.40	24244.79	3	8081.60	16.04
w		5039.93	10	504.00	
t	80592.33	29284.72	13		

$F_{3,10} = 3.71$, with significant difference at the 5% level

Table III-20. Ethylbenzene Removal by GAC after Treatment with 2.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table III-21. Tukey's Test for Data in Table III-20.

For 4 treatment and df(W)=10, Student t at 5% = 4.33
Standard Error = SQR(504.0/4) = 11.22
Least Significant Difference = 11.22 x 4.33 = 48.58
Any two sample means that differ by 16.81 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly differnt from the storage tank readings.
The ClO_2-GAC readings are also significantly lower than the Ozone-GAC and the GAC only readings.

0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
5.0	58.4	45.6	5.0	5.0	
10.0	5.0	5.0	-	51.5	
-	14.5	31.0	10.5	42.5	
15.0	77.9	81.6	15.5	99.0	289.0

	RS	SS	df	MS	F
m		6424.69			
b	7741.95	1317.26	4	329.31	0.71
w		3712.97	8	464.12	
t	11454.92	5030.23	12		

$F_{4,1}$ = 3.84, with no significant difference at the 5% level

Table III-22. Comparing Ethylbenzene Removal by GAC at Various ClO_2 concentration and Contact Time

0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
11.2	27.7	10.0	10.0	5.0	
26.2	10.0	10.0	14.1	10.0	
-	15.1	11.0	10.0	10.0	
37.4	52.8	31.0	34.1	25.0	180.3

	RS	SS	df	MS	F
m		2322.00			
b	2544.93	222.93	4	55.73	1.81
w		307.06	10	30.71	
t	2851.99	529.99	14		

$F_{4,10}$ = 3.48, with no significant difference at the 5% level

Table III-23. Comparing Ethylbenzene Removal by GAC at Various Ozone Concentration and Contact Time

Run #1	# 2	# 3	# 4	# 5	Sum
18.4	10.0	-	-	60.4	
14.6	-	10.0	5.0	10.0	
-	26.8	10.6	52.0	29.4	
-	-	-	-	91.0	
33.0	36.8	20.6	57.0	190.8	338.2

	RS	SS	df	MS	F
m		9531.60			
b	12159.46	2627.86	4	656.97	0.91
w		5045.38	7	720.77	
t	17204.84	7673.24	11		

$F_{4,7} = 4.12$, with no significant difference at the 5% level

Table III-24. Comparing Ethylbenzene Removal by GAC Without any Pre-Oxidation Treatment

	Carbon A (F & I)	Carbon B (G & J)	Sum
ClO_2	5.0	10.0	
	58.4	14.5	
	5.0	5.0	
	45.6	5.0	
	31.0	5.0	
	10.5	42.5	
	51.5	-	
	-	-	
Sum	207.0	82.0	289.0
ave.	29.57	13.67	21.62
Ozone	11.2	26.2	
	27.7	15.1	
	10.0	10.0	
	10.0	10.0	
	11.0	14.8	
	13.3	5.0	
	10.0	10.0	
	10.0	-	
Sum	103.2	91.1	194.3
ave.	12.9	13.0	12.95
ave.	21.24	13.34	ave.=17.29

	RS	SS	df	MS	F
m		8286.73			
a	8802.86	516.13	1	516.13	2.57
b	8719.23	432.50	1	432.50	2.15
ab	9678.88	443.52	1	443.52	2.21
w		4825.45	24	201.06	
t	14504.33	6217.60	27		

$F_{1\ 24} = 4.26$, with no significant difference at the 5% level

Table III-25. Ethylbenzene Removal by Two Different Type of GAC

Storage	Ozone	GAC	Sum
125.1	66.6	10.0	
127.8	51.4	10.0	
128.3	17.1	11.0	
381.2	135.1	31.0	547.3

	RS	SS	df	MS	F
m		33281.92			
b	54842.15	21560.23	2	10780.12	50.04
w		1292.52	6	215.42	
t	56134.67	2285.75	8		

$F_{2,6} = 5.14$, with significant difference at the 5% level

Table III-26. Ethylbenzene Removal by 1.0 mg/L Ozone and Ozone-GAC at 30 minute contact time

Table III-27. Tukey's Test for Data in Table III-26.

For 3 treatment and df(W)=6, Student t at 5% = 4.34
Standard Error = SQR (215.42 / 3) = 8.47
Least Significant Difference = 8.47 x 4.04 = 36.76
Any two sample means that differ by 36.76 or more are significantly different at the 5% level
Conclusion : GAC readings are not significantly different from the Ozone readings

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Storage	Ozone	GAC	Sum
126.7	40.6	10.0	
125.1	65.3	13.3	
125.4	67.6	10.0	
125.1	-	14.8	
502.3	173.5	48.1	723.9

	RS	SS	df	MS	F
m		47639.20			
b	73688.81	26049.61	2	13024.80	222.93
w		467.40	8	58.43	
t	74156.21	26517.01	10		

$F_{2,8} = 4.46$, with significant difference at the 5% level

Table III-28. Ethylbenzene Removal by 1.0 mg/L Ozone and Ozone-GAC at 60 minute contact time

Table III-29. Tukey's Test for Data in Table III-28.

For 3 treatment and df(W)=8, Student t at 5% = 4.04
Standard Error = SQR (58.43/4) = 3.82
Least Significant Difference = 3.82 x 4.04 = 15.43
Any two sample means that differ by 15.43 or more are significantly different at the 5% level
Conclusion : GAC readings are significantly different from the storage tank and Ozone readings

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Storage	Ozone	GAC	Sum
123.7	10.0	5.0	
123.7	10.0	10.0	
126.3	25.3	10.0	
373.7	45.3	25.0	444

	RS	SS	df	MS	F
m		21904.0			
b	47442.93	25538.93	2	12769.47	432.28
w		177.23	6	29.54	
t	47620.16	25716.16	8		

$F_{2,6} = 5.14$, with significant difference at the 5% level

Table III-30. Ethylbenzene Removal by 2.0 mg/L Ozone and GAC at 30 minute contact time

Table III-31. Tukey's Test for Data in Table III-32.

For 3 treatment and df(W)=6, Student t at 5% = 4.34
Standard Error=SQR (29.54 / 3) = 3.14
Least Significant Difference = 3.14 x 4.34 = 13.63
Any two sample means that differ by 13.63 or more are significantly different at the 5% level
Conclusion : GAC readings are not significantly different from the ozone readings

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Storage	Ozone	GAC	Sum
147.6	32.5	-	
125.2	46.1	0.9	
272.8	78.6	0.9	352.3

	RS	SS	df	MS	F
m		24823.06			
b	40299.71	15476.65	2	7738.33	45.07
w		343.36	2	171.68	
t	40643.07	15820.01	4		

$F_{2,4}$ = 19.0, with significant difference at the 5% level

Table III-32. Ethylbenzene Removal by 2.0 mg/L Ozone and GAC at 60 minute contact time

Table III-33. Tukey's Test for Data in Table III-32.

For 3 treatment and df(W)=4, Student t at 5% = 5.00
Standard Error=SQR (171.68/2) = 9.20
Least Significant Difference = 9.20 x 5.00 = 46.0
Any two sample means that differ by 46.0 or more are significantly different at the 5% level
Conclusion : GAC readings are not significantly different from the ozone readings

APPENDIX IV

ANOVA TABLES FOR TOC STUDY

Storage	ClO_2	Ozone	Sum
3.18	3.28	3.15	9.61
3.34	3.41	3.18	9.93
3.99	3.73	3.68	11.40
10.51	10.42	10.01	30.94

	RS	SS	df	MS	F
m		106.36			
b	106.41	0.052	2	0.026	0.24
w		0.65	6	0.11	
t	107.06	0.7	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table IV-1. TOC Reduction by 0.5 mg/L Ozone and ClO_2 at 30 minutes contact time

Storage	ClO_2	Ozone	Sum
3.24	3.22	3.23	9.69
2.83	2.93	2.84	8.60
2.85	2.68	3.29	8.82
8.92	8.83	9.36	27.11

	RS	SS	df	MS	F
m		81.66			
b	81.72	0.055	2	0.027	0.44
w		0.37	6	0.062	
t	82.09	0.43	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table IV-2. TOC Reduction by 0.5 mg/L Ozone and ClO_2 at 60 minutes contact time

	Storage	ClO_2	Ozone	Sum
30 min	3.18	3.28	3.15	
	3.34	3.41	3.18	
	3.99	3.73	3.68	
Sum	10.51	10.42	10.01	30.94
ave.	3.50	3.47	3.34	3.44
60 min	3.24	3.22	3.23	
	2.83	2.93	2.84	
	2.85	2.68	3.29	
Sum	8.92	8.83	9.36	Sum=27.11
ave.	2.97	2.94	3.12	ave.=3.01
Sum	19.42	19.25	19.37	Sum=58.04
ave.	3.24	3.20	3.23	ave.=3.22

	RS	SS	df	MS	F
m		187.21			
a	188.03	0.82	1	0.82	9.42
b	187.21	0.0028	2	0.0014	0.02
ab	188.13	0.098	2	0049	0.53
w		1.03	12	0.086	
t	189.15	1.94	17		

For a, $F_{1\ 12}$= 4.75, with significant difference at the 5% level
For b and ab, $F_{2\ 12}$ = 3.88, with no significant difference at the 5% level

Table IV-3. TOC Reduction by 0.5 mg/L Ozone and ClO_2 at 30 and 60 minutes contact time

Table IV-4. Tukey's Test for data in Table IV-3.

For 6 treatment and df(w)= 12, Student t at 5% = 4.75
Standard Error = SQR(0.086 / 3) = 0.17
Least Difference = 4.75 x 0.17 = 0.81
Any two sample means that differ by 0.81 or more are significantly different at the 5% level
Conclusion : no interaction between the parameters.

Storage	ClO_2	Ozone	Sum
3.70	3.71	3.62	
3.16	3.11	3.55	
3.28	2.80	3.01	
10.14	9.62	10.18	29.94

	RS	SS	df	MS	F
m		99.60			
b	99.67	0.065	2	0.033	0.24
w		0.81	6	0.14	
t	100.48	0.88	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table IV-5. TOC Reduction by 1.0 mg/L Ozone and ClO_2 and 30 minute of contact time

Storage	ClO_2	Ozone	Sum
4.54	3.55	3.71	11.8
3.64	-	3.55	7.19
4.42	2.92	3.13	10.47
12.60	6.47	10.39	29.46

	RS	SS	df	MS	F
m		108.49			
b	109.83	1.34	2	0.67	3.90
w		0.86	5	0.17	
t	110.69	2.20	7		

$F_{2,5} = 5.79$, with no significant difference at the 5% level

Table IV-6. TOC Reduction by 1.0 mg/L Ozone and ClO_2 at 60 minute of contact time

	Storage	ClO_2	Ozone	Sum
30 min	3.70	3.71	3.62	
	3.16	3.11	3.55	
	3.28	2.80	3.01	
Sum	10.14	9.62	10.18	29.94
ave.	3.38	3.21	3.39	3.33
60 min	4.54	3.55	3.71	
	3.64	-	3.55	
	4.42	2.92	3.13	
Sum	12.60	6.47	10.39	29.46
ave.	4.20	3.24	3.46	3.63
ave.	3.79	3.23	3.43	ave.= 3.48

	RS	SS	df	MS	F
m		201.27			
a	201.65	0.38	1	0.38	0.57
b	202.55	1.28	2	0.64	0.96
ab	203.12	0.19	2	0.10	0.15
w		8.05	12	0.67	
t	211.17	9.90	17		

For a, $F_{1\ 12} = 4.75$, with no significant difference at the 5% level
For b and ab, $F_{2\ 12} = 3.88$, with no significant difference at the 5% level

Table IV-7. TOC Redcution by 1.0 mg/L Ozone and ClO_2 at 30 and 60 minutes contact time

Storage	ClO_2	Ozone	Sum
3.47	3.87	3.74	
3.31	3.35	3.51	
3.40	-	3.48	
2.76	3.26	--	
2.43	2.60	2.38	
15.37	13.08	13.11	41.56

	RS	SS	df	MS	F
m		132.87			
b	132.98	0.12	2	0.059	0.21
w		2.77	10	0.28	
t	135.75	2.88	12		

$F_{2\ 10} = 4.10$, with no significant difference at the 5% level

Table IV-8. TOC Reduction by 2.0 mg/L Ozone and ClO_2 and 30 minute of contact time

Storage	ClO_2	Ozone	GAC Only	Sum
3.18	2.02	2.03	1.85	
3.34	1.80	1.63	1.89	
3.99	3.12	1.94	-	
10.51	6.94	5.60	3.74	26.76

	RS	SS	df	MS	F
m		65.25			
b	70.32	5.07	3	1.69	8.05
w		1.46	7	0.21	
t	71.78	6.53	10		

Table IV-9. TOC Reduction by GAC after Pre-Treatment with 0.5 mg/L ClO_2 and Ozone at 30 minute contact time

Table IV-10. Tukey's Test for Data in Table IV-9.

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(0.21/3) = 0.26
Least Significant Difference = 4.68 x 0.26 = 1.22
Any two sample means that differ by 1.22 or more are significantly different at the 5% level
Conclusion : There is significant difference between the Ozone-GAC and GAC-only columns with the storage tank readings.
There is no difference between ClO_2-GAC and storage tank readings.
There is no difference between ClO_2-GAC with Ozone-GAC and GAC-only readings.

Storage	ClO_2	Ozone	GAC Only	Sum
3.24	2.01	2.92	1.73	
2.83	0.70	2.46	-	
2.85	1.31	-	1.39	
8.92	4.02	5.38	3.12	21.44

	RS	SS	df	MS	F
m		45.97			
b	51.25	5.28	3	1.76	9.26
w		1.13	6	0.19	
t	52.38	6.41	9		

$F_{3,6} = 4.76$, with significant difference at the 5% level

Table IV-11. TOC Reduction by GAC afterPre-Treatment with 0.5 mg/L ClO_2 and Ozone at 60 minute contact time

Table IV-12. Tukey's Test for Data in Table IV-11.

For 4 treatment and df(W)=6, Student t at 5% = 4.90
Standard Error = SQR(0.19/3) = 0.25
Least Significant Difference = 0.25 x 4.90 = 1.23
Any two sample means that differ by 1.23 or more are significantly different at the 5% level
Conclusion : Both the ClO_2-GAC and GAC-only systems were effective in lowering the ethylbenzene concentration.
The GAC-Only readings are significantly lowered than the storage tank readings.
There is no significant difference between Ozone-GAC with the storage tank and GAC-only readings.

Storage	ClO_2	Ozone	GAC Only	Sum
3.70	2.23	2.21	-	
3.16	1.33	1.66	1.67	
3.28	1.61	1.73	1.16	
10.14	5.17	5.60	2.83	23.74

	RS	SS	df	MS	F
m		51.24			
b	57.64	6.4	3	2.13	16.35
w		0.9	7	0.13	
t	58.54	7.3	10		

$F_{3,7} = 4.35$, with significant difference at the 5% level

Table IV-13. TOC Reduction by GAC after Treatment with 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table IV-14. Tukey's Test for Data in Table IV-13

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(0.13/3) = 0.21
Least Significant Difference = 0.21 x 4.68 = 0.98
Any two sample means that differ by 0.98 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly different from the storage tank readings

Storage	ClO_2	Ozone	GAC Only	Sum
4.54	1.94	1.78	-	
3.64	-	2.58	2.06	
3.64	-	2.58	-	
4.42	1.58	1.47	1.77	
16.24	3.52	8.41	3.83	32.00

	RS	SS	df	MS	F
m		85.33			
b	97.15	11.82	3	3.94	17.91
w		1.78	8	0.22	
t	98.93	13.60	11		

$F_{3,8} = 4.07$, with significant difference at the 5% level

Table IV-15. TOC Reduction by GAC after Treatment with 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

Table IV-16. Tukey's Test for Data in Table IV-15.
For 4 treatment and df(W)=8, Student t at 5% = 4.53
Standard Error = SQR(0.22 / 4) = 0.23
Least Significant Difference = 0.23 x 4.53 = 1.04
Any two sample means that differ by 1.04 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly different from the storage tank readings

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Storage	ClO_2	Ozone	GAC Only	Sum
3.47	1.88	2.84	1.97	
3.31	1.29	1.71	2.56	
3.40	-	1.85	1.81	
2.76	1.43	-	1.47	
12.94	4.60	6.40	7.81	31.75

	RS	SS	df	MS	F
m		72.00			
b	77.81	5.82	3	1.94	10.2
w		1.89	10	0.19	
t	79.70	7.70	13		

$F_{3,10} = 3.71$, with significant difference at the 5% level

Table IV-17. TOC Reduction by GAC after Treatment with 2.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table IV-18. Tukey's Test for Data in Table IV-17.

For 4 treatment and df(W)= 10, Student t at 5% = 4.33
Standard Error = SQR(0.19/4) = 0.22
Least Significant Difference = 0.22 x 4.33 = 0.95
Any two sample means that differ by 0.95 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without pre-oxidation are significantly different from the storage tank readings.

0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
2.02	2.01	2.23	1.94	1.88	
1.80	0.70	1.33	-	1.29	
3.12	1.31	1.61	1.58	1.43	
6.94	4.02	5.17	3.52	4.60	24.25

	RS	SS	df	MS	F
m		42.00			
b	43.60	1.60	4	0.40	1.43
w		2.54	9	0.28	
t	46.14	4.14	13		

$F_{4,9}$ = 3.63, with no significant difference at the 5% level

Table IV-19. Comparing TOC Reduction by GAC at Various ClO$_2$ concentration and Contact Time

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0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
2.03	2.92	2.21	1.78	2.84	
1.63	2.46	1.66	2.58	1.71	
-	-	-	1.58	-	
1.94	-	1.73	1.47	1.85	
5.60	5.38	5.60	7.41	6.40	30.39

	RS	SS	df	MS	F
m		61.57			
b	62.76	1.19	4	0.30	1.58
w		1.89	10	0.19	
t	64.65	3.08	14		

$F_{4,10} = 3.48$, with no significant difference at the 5% level

Table IV-20. Comparing TOC Redcution by GAC at Various Ozone Concentration and Contact Time

0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
1.85	1.73	-	-	1.97	
1.89	-	1.67	2.06	2.56	
-	1.39	1.16	1.77	1.81	
-	-	-	-	1.47	
3.74	3.12	2.83	3.83	7.81	21.33

	RS	SS	df	MS	F
m		37.91			
b	38.45	0.54	4	0.14	1.17
w		0.85	7	0.12	
t	39.30	1.39	11		

$F_{4,7} = 4.12$, with no significant difference at the 5% level

Table IV-21. Comparing TOC Reduction by GAC Without any Pre-Oxidation Treatment

	Carbon A (F & I)	Carbon B (G & J)	Sum
ClO_2	2.02	1.80	
	2.01	3.12	
	0.70	1.31	
	2.33	1.33	
	1.61	1.94	
	1.58	1.88	
	1.29	1.43	
	-	-	
Sum	11.44	12.81	24.25
ave.	1.63	1.83	1.73
Ozone	2.03	1.63	
	2.92	1.94	
	2.46	1.66	
	2.21	1.78	
	1.73	1.58	
	2.58	2.84	
	1.47	1.85	
	1.71	-	
Sum	17.11	13.28	30.39
ave.	2.14	1.90	2.02
ave.	1.89	1.87	ave.=1.88

	RS	SS	df	MS	F
m		102.21			
a	102.28	0.07	1	0.07	0.27
b	102.22	0.01	1	0.01	0.38
ab	102.63	0.42	1	0.42	1.62
w		6.39	25	0.26	
t	109.02	6.81	28		

$F_{1,25} = 4.24$, with no significant difference at the 5% level

Table IV-22. Comparing TOC Reduction by Two Different Type of GAC

APPENDIX V

ANOVA TABLES FOR COLOUR STUDY

Storage	ClO_2	Ozone	Sum
7	2	1	10.0
3	3	2	8.0
5	4	1	10.0
15.0	9.0	4.0	28.0

	RS	SS	df	MS	F
m		87.11			
b	107.33	20.22	2	10.11	5.68
w		10.67	6	1.78	
t	118.0	30.89	8		

$F_{2,6} = 5.14$, with significant difference at the 5% level

Table V-1. Colour Reduction by 0.5 mg/L ClO_2 and Ozone at 30 minutes contact time

Table V-2. Tukey's Test for data in Table V-1.

For 3 treatment and df(W) = 6, Student t at 5% = 4.34
Standard Error = SQR(1.78/3) = 0.77
Least Difference = 0.77 x 4.34 = 3.34
Any two sample means that differ by 3.34 or more are significantly different at the 5% level
Conclusion: Ozone readings are significantly different from the storage tank and ClO_2 readings

Storage	ClO_2	Ozone	Sum
3	1	2	6.0
5	3	2	10.0
2	1	1	4.0
10.0	5.0	5.0	20.0

	RS	SS	df	MS	F
m		44.44			
b	50.0	5.56	2	2.78	2.09
w		8.0	6	1.33	
t	58.0	13.56	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table V-3. Colour Reduction by 0.5 mg/L ClO_2 and Ozone at 60 minutes contact time

	Storage	ClO_2	Ozone	Sum
30 min	7	2	1	
	3	3	2	
	5	4	1	
Sum	15.0	9.0	4.0	28.0
ave.	5.0	3.0	1.33	3.11
60 min	3	1	2	
	5	3	2	
	2	1	1	
Sum	10.0	5.0	5.0	Sum=20.0
ave.	3.33	1.67	1.67	ave.=2.22
Sum	25.0	14.0	9.0	Sum=48.0
ave.	4.2	2.3	1.5	ave.=2.67

	RS	SS	df	MS	F
m		128.32			
a	131.40	3.08	1	3.08	1.97
b	152.19	23.87	2	11.94	7.65
ab	157.31	28.99	2	14.49	9.29
w		18.69	12	1.56	
t	176.0	47.68	17		

For a, $F_{1,12} = 4.75$, with no significant difference at the 5% level
For b and ab, $F_{2,12} = 3.88$, with significant difference at the 5% level

Table V-4. Colour Reduction by 0.5 mg/L ClO_2 and Ozone at 30 and 60 minutes Contact Time

Table V-5. Tukey's Test for Data in Table V-4.
For 6 treatment and df(W)= 12, Student t at 5% = 4.75
Standard Error = SQR (1.56 / 3) = 0.72
Least Significant difference = 0.72 x 4.75 = 3.42
Any two sample means that differ by 3.42 or more are significantly different at the 5% level
Conclusion: Ozone readings are significantly different from the storage tank and ClO_2 readings at 30 minute contact time, and no difference at 60 minute contact time

Storage	ClO_2	Ozone	Sum
3	1	1	
2	1	1	
4	2	2	
9.0	4.0	4.0	17.0

	RS	SS	df	MS	F
m		32.1			
b	37.67	5.57	2	2.79	5.03
w		3.33	6	0.56	
t	41.0	8.9	8.0		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table V-6. Colour Reduction by 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

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Storage	ClO_2	Ozone	Sum
4	2	1	
4	-	2	
4	3	1	
12.0	5.0	4.0	21.0

	RS	SS	df	MS	F
m		55.13			
b	65.83	10.7	2	5.35	23.26
w		1.17	5	0.23	
t	67.0	11.87	7		

$F_{2,5} = 5.79$, with significant difference at the 5% level

Table V-7. Colour Reduction by 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

Table V-8. Tukey's Test for Data in Table V-7.

For 3 treatment and df(W)=5, Student t at 5%=4.54
Standard Error = SQR (0.23/3) = 0.28
Least Significant Difference = 0.28 x 4.54 = 1.27
Any two sample means that differ by 1.27 or more are significantly different at the 5% level
Conclusion : Ozone and ClO_2 readings are significantly different from the storage tank readings

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	Storage	ClO_2	Ozone	Sum
30 min	3	1	1	
	2	1	1	
	4	2	2	
Sum	9.0	4.0	4.0	17.0
ave.	3.0	1.33	1.33	1.89
60 min	4	2	1	
	4	-	2	
	4	3	1	
Sum	12.0	5.0	4.0	
ave.	4.0	2.5	1.3	2.61
ave.	3.5	1.92	1.3	ave.=2.25

	RS	SS	df	MS	F
m		84.14			
a	86.29	2.15	1	2.15	3.56
b	98.09	13.95	2	6.98	11.44
ab	101.26	17.12	2	8.56	14.03
w		6.74	11	0.61	
t	108.0	23.86	16		

For a, $F_{1,11} = 4.84$, with no significant difference at the 5% level
For b and ab, $F_{2,11} = 3.98$, with significant difference at the 5% level

Table V-9. Colour reduction by 1.0 mg/L ClO_2 and Ozone at 30 and 60 minutes contact time

Table V-10. Tukey's Test for data in Table V-9.

For 6 treatment and df(w)= 11, Student t at 5% = 4.82
Standard Error = SQR (0.61 / 3) = 0.45
Least Difference = 0.45 x 4.82 = 2.17
Any two sample means that differ by 2.17 or more are significantly different at the 5% level
Conclusion : Significant difference exist between post-ozonation readings at 60 minute level with post-ClO_2 treatment and storage tank readings.
No significant difference exist in the 30 minute contact time readings

---

Storage	ClO_2	Ozone	Sum
4	2	1	
2	1	0.5	
1	-	1	
3	2	-	
4	4	3	
14.0	9.0	5.5	28.5

	RS	SS	df	MS	F
m		62.48			
b	67.01	4.53	2	2.27	1.49
w		15.24	10	1.52	
t	82.25	19.77	12		

$F_{2,10} = 4.10$, with no significant difference at the 5% level

Table V-11. Colour Reduction by 2.0 mg / L ClO_2 and Ozone at 30 minute of contact time

---

Storage	ClO_2	Ozone	GAC Only	Sum
7	1	1	1	
3	1	0.5	0.5	
5	2	1	1	
15.0	4.0	2.5	2.5	24.0

	RS	SS	df	MS	F
m		48.0			
b	84.5	36.5	3	12.17	10.77
w		9.0	8	1.13	
t	93.5	45.5	11		

$F_{3,8} = 4.07$, with significant difference at the 5% level.

Table V-12. Colour Reduction by GAC after treatment with 0.5 mg/L ClO_2 and Ozone at 30 minute contact time

Table V-13. Tukey s Test for Data in Table V-12.

For 4 treatment and df(W)=8, Student t at 5% = 4.53
Standard Error = SQR(1.13 / 3) = 0.61
Least Significant Difference = 4.53 x 0.61 = 2.76
Any two sample means that differ by 2.76 or more are significantly different at the 5% level
Conclusion. There is significant difference between all GAC readings, with or without pre-oxidation, from the storage tank readings.

Storage	ClO_2	Ozone	GAC Only	Sum
3	1	1	1	
5	1	1	-	
2	0	-	1	
10.0	2.0	2.0	2.0	16.0

	RS	SS	df	MS	F
m		25.6			
b	37.17	11.53	3	3.86	3.39
w		6.83	6	1.14	
t	44.0	18.4	9		

$F_{3,6}$ = 4.76, with no significant difference at the 5% level

Table V-14. Colour Reduction by GAC after Treatment with 0.5 mg/L ClO_2 and Ozone at 60 minute contact time

Storage	ClO_2	Ozone	GAC Only	Sum
3	1	1	-	
2	1	1	1	
4	1	1	1	
9.0	3.0	3.0	2.0	17.0

	RS	SS	df	MS	F
m		26.27			
b	35.0	8.73	3	2.91	10.03
w		2.0	7	0.29	
t	37.0	10.73	10		

$F_{3,7}$ = 4.35, with significant difference at the 5% level

Table V-15. Colour Reduction by GAC after Treatment with 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table V-16. Tukey's Test for Data in Table V-15.

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(0.29/3) = 0.31
Least Significant Difference = 0.31 x 4.68 = 1.45
Any two sample means that differ by 1.45 or more are significantly different at the 5% level
Conclusion: GAC readings, with or without oxidation are significantly different from the storage tank readings

Storage	ClO_2	Ozone	GAC Only	Sum
4	1	1	-	
4	-	1	1	
4	-	3	-	
4	1	1	1	
12.0	2.0	6.0	2.0	22.0

	RS	SS	df	MS	F
m		40.33			
b	49.0	8.67	3	2.89	0.75
w		31.0	8	3.88	
t	80.0	39.67	11		

$F_{3,8} = 4.07$, with no significant difference at the 5% level

Table V-17. Colour Reduction by GAC after Treament with 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

---

Storage	ClO_2	Ozone	GAC Only	Sum
4	-	1	1	
2	0.5	0.5	1	
1	-	1	3	
3	0.0	-	1	
10.0	0.5	2.5	6.0	19.0

	RS	SS	df	MS	F
m		27.77			
b	36.21	8.44	3	2.81	3.05
w		8.29	9	0.92	
t	44.50	16.73	12		

$F_{3,9} = 3.86$, with no significant difference at the 5% level

Table V-18. Colour Reduction by GAC after Treatment with 2.0 mg/L ClO_2 and Ozone at 30 minute contact time

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0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	
1	1	1	1	0.5	
1	1	1	-	-	
2	0.0	1	1	0.0	
4.0	2.0	3.0	2.0	0.5	11.5

	RS	SS	df	MS	F
m		10.17			
b	11.79	1.62	4	0.41	2.57
w		1.46	9	0.16	
t	13.25	3.08	13		

$F_{4,9} = 3.63$, with no significant difference at the 5% level

Table V-19. Comparing Colour Reduction by GAC at Various ClO_2 Concentration and Contact Time

---

0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
1	1	1	1	1	
0.5	1	1	1	0.5	
1	-	1	1	1	
-	-	-	3	-	
2.5	2.0	3.0	6.0	2.5	16.0

	RS	SS	df	MS	F
m		17.07			
b	18.17	1.10	4	0.28	0.85
w		3.33	10	0.33	
t	21.5	4.43	14		

For $F_{4,10} = 3.48$, with no significant difference at the 5% level

Table V-20. Comparing Colour Reduction by GAC Columns after Various Pre-Ozonation Dosage and Contact Time

Run #	1	# 2	# 3	# 4	# 5	Sum
	1	1	-	-	1	
	0.5	-	1	1	1	
	1	1	1	1	3	
	-	-	-	-	1	
	2.5	2.0	2.0	2.0	6.0	14.5

	RS	SS	df	MS	F
m		16.17			
b	17.08	0.91	4	0.23	0.58
w		3.17	8	0.40	
t	20.25	4.08	12		

$F_{4,8} = 3.84$, with no significant difference at the 5% level

Table V-21. Comparing Colour Reduction by GAC Without any Pre-Oxidation Treatment

	Carbon A (F & I)	Carbon B (G & J)	Sum
ClO_2	1	1	
	1	2	
	1	0	
	1	1	
	1	1	
	1	0	
	0.5	-	
	-		
Sum	6.5	5.0	11.5
ave.	0.93	0.83	0.88
Ozone	1	0.5	
	1	1	
	1	1	
	1	1	
	1	3	
	1	1	
	1	1	
	0.5	-	
Sum	7.5	8.5	16.0
ave.	0.94	1.22	1.08
ave.	0.94	1.03	ave.=0.98

	RS	SS	df	MS	F
m		26.62			
a	26.90	0.28	1	0.28	0.90
b	26.95	0.33	1	0.33	1.06
ab	27.21	0.59	1	0.51	1.65
w		7.54	24	0.31	
t	34.75	8.13	27		

$F_{1\ 24} = 4.26$, with no significant difference at the 5% level

Table V-22. Colour Reduction by Two Different Type of GAC

Storage	Ozone	GAC	Sum
7	1	1	
3	2	0.5	
5	1	1	
15.0	4.0	2.5	21.5

	RS	SS	df	MS	F
m		51.36			
b	82.42	31.06	2	15.53	14.06
w		8.83	6	1.47	
t	91.25	39.89	8		

$F_{2,6} = 5.14$, with significant difference at the 5% level

Table V-23. Colour Reduction by 0.5 mg/L Ozone and GAC at 30 minutes contact time

Table V-24. Tukey's Test for data in Table V-23.

For 3 treatment and df(W) = 6, Student t at 5% = 4.34
Standard Error = SQR(1.43/3) = 0.70
Least Difference = 0.70 x 4.34 = 3.04
Any two sample means that differ by 3.04 or more are significantly different at the 5% level
Conclusion: GAC readings are not significantly different from the ozone readings

APPENDIX VI

ANOVA TABLES FOR TURBIDITY STUDY

Storage	ClO_2	Ozone	Sum
3.0	2.9	3.1	
4.4	3.6	3.4	
4.6	3.9	3.7	
12.0	10.4	10.2	32.6

	RS	SS	df	MS	F
m		118.08			
b	118.73	0.65	2	0.32	0.87
w		2.23	6	0.37	
t	120.96	2.88	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table VI-1. Turbidity Reduction by 0.5 mg/L ClO_2 and Ozone at 30 minutes contact time

Storage	ClO_2	Ozone	Sum
3.0	2.5	3.0	
4.6	3.4	3.5	
3.3	2.5	2.4	
10.9	8.4	7.8	27.1

	RS	SS	df	MS	F
m		81.60			
b	83.40	1.80	2	0.90	2.43
w		2.23	6	0.37	
t	85.63	4.03	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table VI-2. Turbidity Reduction by 0.5 mg/L ClO_2 and Ozone at 60 minutes contact time

	Storage	ClO_2	Ozone	Sum
30 min	3.0	2.9	3.1	
	4.4	3.6	3.4	
	4.6	3.9	3.7	
Sum	12.0	10.4	10.2	32.6
60 min	3.0	2.5	3.0	
	4.6	3.4	3.5	
	3.3	2.5	2.4	
Sum	10.9	8.4	8.9	Sum=28.2
Sum	22.9	18.8	19.1	Sum=60.8

	RS	SS	df	MS	F
m		205.37			
a	206.44	1.08	1	1.08	2.16
b	207.11	1.74	2	0.87	1.75
ab	208.26	0.074	2	0.037	0.075
w		5.97	12	0.50	
t	213.08	7.71	17		

For a, $F_{1,12} = 4.75$, with no significant difference at the 5% level
For b and ab, $F_{2,12} = 3.88$, with no significant difference at the 5% level

Table VI-3. Turbidity Reduction by 0.5 mg/L ClO_2 and Ozone at 30 and 60 minutes contact time

Storage	ClO_2	Ozone	Sum
3.5	3.4	3.0	
3.5	3.4	3.4	
4.2	3.9	3.7	
11.2	10.7	10.1	32.0

	RS	SS	df	MS	F
m		113.78			
b	113.98	0.20	2	0.10	0.82
w		0.74	6	0.12	
t	114.72	0.94	8		

$F_{2,6} = 5.14$, with no significant difference at the 5% level

Table VI-4. Turbidity Reduction by 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Storage	ClO_2	Ozone	Sum
3.9	3.1	3.1	
3.4	-	3.0	
4.2	3.4	3.3	
11.5	6.5	9.4	27.4

	RS	SS	df	MS	F
m		93.85			
b	94.66	0.82	2	0.41	4.88
w		0.42	5	0.084	
t	95.08	1.23	7		

$F_{2,5} = 5.79$, with no significant difference at the 5% level

Table VI-5. Turbidity Reduction by 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

	Storage	ClO_2	Ozone	Sum
30 min.	3.5	3.4	3.0	
	3.5	3.4	3.4	
	4.2	3.9	3.7	
Sum	11.2	10.7	10.1	32.0
ave.	3.73	3.57	3.37	3.56
60 min.	3.9	3.1	3.1	
	3.4	-	3.0	
	4.2	3.4	3.3	
Sum	11.5	6.5	9.4	27.4
ave.	3.83	3.25	3.13	3.41
ave.	3.78	3.41	3.25	ave.=3.48

	RS	SS	df	MS	F
m		201.33			
a	201.37	0.037	1	0.037	0.054
b	202.13	0.79	2	0.40	0.58
ab	202.34	0.17	2	0.087	0.13
w		7.47	11	0.68	
t	209.80	8.47	16		

For a, $F_{1,11} = 4.84$, with no significant difference at the 5% level
For b and ab, $F_{2,11} = 3.98$, with no significant difference at the 5% level

Table VI-6. Turbidity Reduction by 1.0 mg/L ClO_2 at 30 and 60 minutes contact time

Storage	ClO_2	Ozone	Sum
35	32	36	
31	30	30	
66	-	55	
26	24	-	
27	25	26	
185.0	111.0	147.0	443.0

	RS	SS	df	MS	F
m		15096.08			
b	15327.50	231.42	2	115.71	0.70
w		1641.50	10	164.15	
t	16969.00	1872.92	12		

$F_{2,10} = 4.10$, with no significant difference at the 5% level

Table VI-7. Turbidity Reduction by 2.0 mg/L ClO_2 and Ozone at 30 minute of contact time

Storage	ClO_2	Ozone	GAC Only	Sum
3.0	0.31	0.31	0.51	
4.4	1.5	0.45	0.70	
4.6	2.1	1.6	-	
12.0	3.91	2.36	1.21	19.48

	RS	SS	df	MS	F
m		34.50			
b	55.68	21.18	3	7.06	11.77
w		4.20	7	0.60	
t	59.88	25.38	10		

$F_{3,7} = 4.35$, with significant difference at the 5% level

Table VI-8. Turbidity Reduction by GAC after Treatment with 0.5 mg/L ClO_2 and Ozone at 30 minute contact time

Table VI-9. Tukey Test for Data in Table VI-8.

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(0.60 / 3) = 0.44
Least Significant Difference = 0.44 x 4.68 = 2.06
Any two sample means that differ by 2.06 or more are significantly different at the 5% level
Conclusion : Ozone-GAC and GAC-Only readings are significantly different from the storage tank and ClO_2-GAC readings.

Storage	ClO_2	Ozone	GAC Only	Sum
3.0	0.55	0.36	0.85	
4.6	0.51	0.55	-	
3.3	0.87	-	0.55	
10.90	1.93	0.91	1.40	15.14

>	RS	SS	df	MS	F
m		22.92			
b	42.24	19.32	3	6.44	23.85
w		1.59	6	0.27	
t	43.83	20.91	9		

$F_{3,6} = 4.76$, with significant difference at the 5% level

Table VI-10. Turbidity Reduction by GAC after Treatment with 0.5 mg/L ClO_2 and Ozone at 60 minute contact time

Table VI-11: Tukey Test for Data in Table VI-10.

For 4 treatment and df(W)=6, Student t at 5% = 4.90
Standard Error = SQR(0.27/3) = 0.30
Least Significant Difference = 0.30 x 4.90 = 1.47
Any two sample means that differ by 1.47 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly different from the storage tank readings.

Storage	ClO_2	Ozone	GAC Only	Sum
3.5	0.51	0.49	-	
3.5	1.0	1.6	0.64	
4.2	0.43	0.31	0.35	
11.2	1.94	2.40	0.99	16.53

	RS	SS	df	MS	F
m		24.84			
b	45.48	20.64	3	6.88	31.27
w		1.53	7	0.22	
t	47.01	22.17	10		

$F_{3,7} = 4.35$, with significant difference at the 5% level

Table VI-12. Turbidity Reduction by GAC after Treatment with 1.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table VI-13. Tukey Test for Data in Table VI-12.

For 4 treatment and df(W)=7, Student t at 5% = 4.68
Standard Error = SQR(0.22 / 3) = 0.27
Least Significant Difference = 0.27 x 4.68 = 1.26
Any two sample means that differ by 1.26 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly different from the storage tank readings.

Storage	ClO_2	Ozone	GAC Only	Sum
3.9	1.94	1.78	-	
3.4	-	0.50	1.0	
4.2	0.23	0.21	0.49	
3.4	-	0.84	-	
14.9	2.17	3.33	1.49	21.89

	RS	SS	df	MS	F
m		39.93			
b	61.74	21.81	3	7.27	16.91
w		3.45	8	0.43	
t	65.19	25.26	11		

$F_{3,8} = 4.07$, with significant difference at the 5% level

Table VI-14. Turbidity Reduction by GAC after Treatment with 1.0 mg/L ClO_2 and Ozone at 60 minute contact time

Table VI-15. Tukey Test for Data in Table VI-14.
For 4 treatment and df(W)=8, Student t at 5% = 4.53
Standard Error = SQR(0.43 / 4) = 0.33
Least Significant Difference = 0.33 x 4.53 = 1.49
Any two sample means that differ by 1.49 or more are significantly different at the 5% level
Conclusion : GAC readings, with or without oxidation are significantly different from the storage tank readings

Storage	ClO_2	Ozone	GAC Only	Sum
35	4	3	3	
31	4	3	3	
66	-	5	8	
26	5	-	6	
158.0	13.0	11.0	20.0	202.0

	RS	SS	df	MS	F
m		2914.48			
b	6437.67	3523.09	3	1174.36	11.76
w		998.33	10	99.84	
t	7436.0	4521.42	13		

$F_{3,10} = 3.71$ with significant difference at the 5% level

Table VI-16. Turbidity Reduction by GAC Columns after Treatment with 2.0 mg/L ClO_2 and Ozone at 30 minute contact time

Table VI-17. Tukey Test for Data in Table VI-16.

For 4 treatment and df(W)=10, Student t at 5% = 4.33
Standard Error = SQR(99.84 / 4) = 5.00
Least Significant Difference = 5.00 x 4.33 = 21.65
Any two sample means that differ by 21.65 or more are significantly different at the 5% level
Conclusion: GAC readings, with or without oxidation are significantly different from the storage tank readings.

0.5 / 30	0.5 / 60	1.0 / 30	1.0 / 60	2.0 / 30	Sum
0.31	0.55	0.51	1.94	4.0	
1.5	0.51	1.0	-	4.0	
2.1	0.87	0.43	0.23	5.0	
3.91	1.93	1.94	2.17	13.0	22.95

	RS	SS	df	MS	F
m		37.62			
b	66.28	28.66	4	7.17	15.93
w		4.06	9	0.45	
t	70.34	32.72	13		

$F_{4,9}$ = 3.84 with significant difference at the 5% level

Table VI-18. Turbidity Reduction by GAC at Various ClO_2 concentration and Contact Time

Table VI-19. Tukey Test for Data in Table VI-18.

For 5 treatment and df(w) = 9, Student t at 5% = 3.48
Standard Error = SQR(0.42 / 3) = 0.37
Least Significant Different = 3.48 x 0.37 = 1.29
Any two sample means that differ by 1.29 or more, are significantly different at the 5% level
Conclusion: The GAC reading with 2.0 mg/L oxidant is significantly different from all other readings.

0.5/30	0.5/60	1.0/30	1.0/60	2.0/30	Sum
0.31	0.36	0.49	1.78	3	
0.45	0.55	1.6	0.50	3	
1.6	-	0.31	0.21	5	
-	-	-	0.84	-	
2.36	0.91	2.40	3.33	11.0	20.0

	RS	SS	df	MS	F
m		26.67			
b	47.30	20.63	4	5.16	8.46
w		6.06	10	0.61	
t	53.36	26.69	14		

$F_{4,10}$ = 3.48, with significant difference at the 5% level

Table VI-20. Turbidity Reduction by GAC at Various Ozone Concentration and Contact Time

Table VI-21. Tukey Test For Data in Table VI-20

For 5 treatment and df(W) = 10, Student t at 5% = 4.66
Standard Error = SQR(0.61/4) = 0.39
Least Significant Different = 0.39 x 4.66 = 1.82
Any two sample means that differ by 1.82 or more, are significantly different at the 5% level
Conlusion: GAC reading after treatment with 2.0 mg/L Ozone are significantly different from all other readings

Run # 1	# 2	# 3	# 4	# 5	Sum
0.51	0.85	-	-	3	
0.70	-	0.64	1.0	3	
-	0.55	0.35	0.49	8	
-	-	-	-	6	
1.21	1.40	0.99	1.49	20.0	25.09

	RS	SS	df	MS	F
m		52.46			
b	103.31	50.85	4	12.71	4.87
w		18.24	7	2.61	
t	121.55	69.09	11		

$F_{4,7}$ = 4.12, with significant difference at the 5% level

Table VI-22. Turbidity Reduction by GAC Without any Pre-Oxidation Treatment

Table VI-23. Tukey Test for Data in Table VI-22

For 5 treatmentand df(W) = 7, Student t at 5%: = 5.06
Standard Error = SQR (2.61 / 4) = 0.81
Least Significant Different = 0.81 x 5.06 = 4.10
Any sample means that differ by 4.10 or more, are significantly different at the 5% level
Conclusion: GAC Run #5 are significantly different from all other readings

	Carbon A (F & I)	Carbon B (G & J)	Sum
ClO_2	0.31	1.5	
	0.55	2.1	
	0.51	0.87	
	0.51	1.0	
	0.43	1.94	
	0.23	4.0	
	4.0	5.0	
Sum	6.54	16.41	
ave.	0.93	2.34	1.64
Ozone	0.31	0.45	
	0.36	1.6	
	0.55	1.6	
	0.49	1.78	
	0.31	0.84	
	0.5	3	
	0.21	5	
	3		
Sum	5.73	14.27	
ave.	0.72	2.04	1.38
ave.	0.83	2.19	ave.=1.51

	RS	SS	df	MS	F
m		66.16			
a	66.66	0.50	1	0.50	0.29
b	79.73	13.57	1	13.57	7.72
ab	80.24	14.08	1	14.08	8.07
w		43.45	25	1.74	
t	123.69	57.53	28		

$F_{1,25} = 4.24$, with significant difference at the 5% levelfor factor b and ab

Table VI-24. Turbidity Reduction by Two Different Type of GAC

Table VI-25. Tukey Test for Data in Table VI-24

For 4 treatment and df(W)=25, Student t at 5% = 3.90
Standard Error = SQR(1.74 / 8) = 0.47
Least Significant Different = 0.47 x 3.90 = 1.83
Any sample means that differ by 1.83 or more, are significantly different at the 5% level
Conclusion: ClO_2-GAC carbon B gave significantly higher turbidity readings than O_3-GAC carbon A.

APPENDIX VII

Table VII-1 Data From Pilot Plant Study

D/M 1983	Parameters	Storage Water	Post ClO_2	ClO_2 GAC	Post O_3	O_3 GAC	Post GAC
25/8	0.5/30 mg/L-min						
	pH	7.7	7.7	8.4	7.8	8.8	8.9
	Temp. C°	19.0	19.5	20.0	19.5	20.0	19.5
	Turbidity NTU	3.0	2.9	0.31	3.1	0.31	0.51
	Colour TCU	7	2	1	1	1	1
	TOC mg/L	3.18	3.28	2.02	3.15	2.03	1.85
	Ethylbenzene ug/L	127	113	ND	125	11	18
24/8	0.5/30 mg/L-min						
	pH	7.9	7.9	9.2	7.9	9.2	9.1
	Temp. C°	19.0	19.0	19.5	20.0	20.0	20.0
	Turbidity NTU	4.4	3.6	1.5	3.4	0.45	0.70
	Colour TCU	3	3	1	2	<1	<1
	TOC mg/L	3.34	3.41	3.12	3.68	1.94	-
	Ethylbenzene ug/L	125	163	<10	150	26	15
23/8	0.5/60 mg/L-min						
	pH	7.6	7.6	8.3	7.7	8.7	9.0
	Temp. C°	18.0	19.0	19.5	19.5	19.5	19.0
	Turbidity NTU	3.0	2.5	0.55	3.0	0.36	0.85
	Colour TCU	3	1	1	2	1	1
	TOC mg/L	3.24	3.22	2.01	3.23	2.92	1.75
	Ethylbenzene ug/L	127	132	58	117	28	<10
15/8	0.5/60 mg/L-min						
	pH	8.1	7.9	8.1	8.0	8.4	-
	Temp. C°	20.5	20.5	21.0	21.0	21.0	-
	Turbidity NTU	4.6	3.4	0.51	3.5	0.55	-
	Colour TCU	5	3	1	2	1	-
	TOC mg/L	2.83	2.93	0.70	2.84	2.46	-
	Ethylbenzene ug/L	126	81	ND	88	<10	-
31/8	0.5/60 mg/L-min						
	pH	7.7	7.7	9.0	7.8	-	8.7
	Temp. C°	19.0	19.5	20.0	20.0	-	19.5
	Turbidity NTU	3.3	2.5	0.87	2.4	-	0.55
	Colour TCU	2	1	0	1	-	1
	TOC mg/L	2.85	2.68	1.31	3.29	-	1.39
	Ethylbenzene ug/L	123	50	15	81	15	27
17/8	1.0/30 mg/L-min						
	pH	7.7	7.7	8.6	7.8	8.6	-
	Temp. C°	20.0	20.0	20.5	20.5	21.0	-
	Turbidity NTU	3.5	3.4	51.0	3.0	0.49	-
	Colour TCU	3	1	1	1	1	-
	TOC mg/L	3.70	3.71	2.23	3.62	2.21	-
	Ethylbenzene ug/L	125	138	46	67	<10	-

D/M 1983	Parameters	Storage Water	Post ClO_2	ClO_2 GAC	Post O_3	O_3 GAC	Post GAC
26/8	1.0/30 mg/L-min						
	pH	7.8	7.7	8.1	7.8	8.9	8.9
	Temp. C°	18.5	19.0	20.0	19.0	19.0	19.0
	Turbidity NTU	3.5	3.4	1.0	3.4	1.61	0.64
	Colour TCU	2	1	1	1	1	1
	TOC mg/L	3.16	3.11	1.33	3.55	1.66	1.67
	Ethylbenzene ug/L	128	-	ND	51	<10	10
30/8	1.0/30 mg/L-min						
	pH	7.8	7.8	8.5	7.9	8.9	8.8
	Temp. C°	19.0	19.0	19.5	19.5	19.5	20.0
	Turbidity NTU	4.2	3.9	0.43	3.7	0.31	0.35
	Colour TCU	4	2	1	2	1	1
	TOC mg/L	3.28	2.8	1.61	3.01	1.33	1.16
	Ethylbenzene ug/L	128	113	31	17	11	11
18/8	1.0/60 mg/L-min						
	pH	7.9	7.9	9.4	8.0	9.3	-
	Temp. C°	19.5	19.5	19.5	20.0	20.0	-
	Turbidity NTU	3.9	3.1	1.94	3.1	1.78	-
	Colour TCU	4	2	1	1	1	-
	TOC mg/L	4.54	3.55	1.94	3.71	1.78	-
	Ethylbenzene ug/L	127	79	ND	41	<10	-
19/8	1.0/60 mg/L-min						
	pH	7.7	-	-	7.8	9.0	9.4
	Temp. C°	17.0	-	-	17.8	18.0	17.5
	Turbidity NTU	3.4	-	-	3.0	0.50	1.0
	Colour TCU	4	-	-	2	1	1
	TOC mg/L	3.64	-	-	3.55	2.58	2.06
	Ethylbenzene ug/L	125	-	-	65	13	ND
29/8	1.0/60 mg/L-min						
	pH	7.8	7.7	8.4	7.9	8.9	8.8
	Temp. C°	18.0	18.0	19.0	19.0	19.0	18.5
	Turbidity NTU	4.2	3.4	0.23	3.3	0.21	0.49
	Colour TCU	4	3	1	1	1	1
	TOC mg/L	4.42	2.92	1.58	3.13	1.47	1.77
	Ethylbenzene ug/L	125	154	11	68	<10	52
13/9	2.0/30 mg/L-min						
	pH	7.7	7.8	8.4	8.0	8.6	8.5
	Temp. C°	13.5	14.5	28.0	16.5	28.0	19.0
	Turbidity NTU	37.0	34.0	4.0	37.0	3.0	3.0
	Colour TCU	4	2	-	<1	<1	<1
	TOC mg/L	3.47	3.87	1.88	0.41	2.84	1.97
	Ethylbenzene ug/L	124	105	ND	<10	ND	60

D/M 1983	Parameters	Storage Water	Post ClO_2	ClO_2 GAC	Post O_3	O_3 GAC	Post GAC
12/9	2.0/30 mg/L-min						
	pH	7.8	7.8	8.2	7.9	9.1	8.5
	Temp. C°	13.3	14.5	20.0	17.5	21.0	21.0
	Turbidity NTU	29.5	30.0	4.0	30.0	3.0	3.0
	Colour TCU	2	1	<1	1	<1	1
	TOC mg/L	3.31	3.35	1.29	3.51	1.71	2.56
	Ethylbenzene ug/L	124	140	52	<10	<10	<10
8/9	2.0/30 mg/L-min						
	pH	7.8	7.8	9.0	-	-	8.9
	Temp. C°	13.5	14.0	13.5	-	-	14.5
	Turbidity NTU	27.0	25.0	5.0	-	-	6.0
	Colour TCU	3	2	0	-	-	1
	TOC mg/L	2.76	3.26	1.43	-	-	1.47
	Ethylbenzene ug/L	128	131	43	-	-	29
9/9	2.0/30 mg/L-min						
	pH	7.7	-	-	7.7	8.8	9.0
	Temp. C°	12.5	-	-	14.0	14.5	13.5
	Turbidity NTU	66.0	-	-	55.0	5.0	8.0
	Colour TCU	1	-	-	1	1	3
	TOC mg/L	3.40	-	-	3.48	1.85	1.81
	Ethylbenzene ug/L	126	-	-	25	<10	91
7/12	1.0/30 mg/L-min						
	pH	7.8	7.8	8.0	-	-	8.6
	Temp. C°	12.5	13.0	24.5	-	-	16.5
	Turbidity NTU	5.4	5.0	0.9	-	-	0.7
	Colour TCU	1	1	1	-	-	1
	TOC mg/L	2.38	2.63	1.35	-	-	1.29
	Ethylbenzene ug/L	123	109	<10	-	-	ND
6/12	1.0/30 mg/L-min						
	pH	7.7	7.8	-	7.7	7.9	8.3
	Temp. C°	13.0	13.3	-	14.5	17.0	15.0
	Turbidity NTU	6.7	6.5	-	5.9	0.40	1.30
	Colour TCU	2	1	-	2	0	1
	TOC mg/L	2.31	3.19	-	2.86	1.25	1.20
	Ethylbenzene ug/L	124	96	-	93	<10	<10
8/12	1.0/30 mg/L-min						
	pH	7.7	-	-	7.6	7.5	8.3
	Temp. C°	13.3	-	-	13.5	17.9	15.0
	Turbidity NTU	4.5	-	-	3.6	1.0	1.3
	Colour TCU	1	-	-	1	1	1
	TOC mg/L	2.30	-	-	-	1.07	1.20
	Ethylbenzene ug/L	124	-	-	110	<10	<10